THEORETICAL CONSIDERATIONS AND EXPERIMENTAL COMPARISONS OF SEVERAL FIGURES OF MERIT FOR A VARIETY OF ATOMIC PLASMA SPECTROSCOPIC TECHNIQUES

BY

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The techniques of pattern recognition are proposed as being able to bring together any analytical problem with an existing suitable analytical technique. An example of the analytical capabilities of pattern recognition is given via the descrimination of the geographical origins of frozen concentrated orange juice by looking at the trace metal content of five selected fingerprinting elements (barium, boron, manganese, gallium and rubidium). The focal point of the problem is determined to be the recognition and development of suitable descriptors to be used in the pattern recognition problem. To this end, outlines for developing numerical estimates of such descriptors as

linear dynamic range, cost of analysis, time of analysis and selectivity are given. Experimental verification of the theoretical definition of selectivity is given by the analysis of several elements in a simulated sea water matrix via atomic absorption and atomic emission spectrometric techniques. The final descriptor proposed is a theoretically calculated limit of detection. Although perhaps of limited use in the pattern recognition problem, theoretically calculated limits of detection afford the analytical chemist a means by which to objectively compare ultimate capabilities of a variety of spectroscopic techniques. Through signal-to-noise (S/N) expressions, limits of detection are calculated for atomic fluorescence spectrometry, atomic absorption spectrometry, atomic emission spectrometry, optoacoustic spectroscopy and optogalvanic spectroscopy. After identifying the limiting noise sources for these techniques, the S/N expressions are solved for the limiting observable concentration (in atoms/cm^3) under a variety of experimental conditions. Two-photon processes are also considered (via virtual and real levels) for atomic fluorescence spectrometry and optogalvanic spectroscopy. Furthermore, the means by which one can convert the detection limit in atoms/cm^3 of hot gases to μg/ml (ppm) of analyte in solution are given. Comparisons of the theoretical limits of detection to experimentally derived limits of detection are made at which time good agreement between the two is observed.

INTRODUCTION

Analytical chemistry is guided on its course to ever increasing sensitivity and selectivity by various technological advances. Accompanying the improvements of this discipline as a science are the rising costs of instrumentation and analysis. No longer can the chemist afford himself to take too many "educated guesses" while trying to solve an analytical problem. It would, therefore, be of great economic importance if the analytical chemist possessed a systematic and objective means of forecasting the utility of a particular analytical technique to solving a specific problem at hand. In general, the approach taken is a purely subjective one based predominantly on the personal experiences of the analyst. Although perfectly adequate at times, there are many disadvantages to relying solely upon a chemist's intuition. If we consider the rapidity with which new techniques and methodologies enter the scientific literature, it becomes virtually impossible to keep abreast of the latest advancements, much less draw objective conclusions concerning their suitability. The problems associated with the bringing together of appropriate analytical methodologies with analytical problems can be classified as part of a more universal concern,

namely, the storage, transferrence and utilization of large amounts of information. To this end, man has developed the modern day computer. However, the computer is rendered useless unless adequate descriptors of the information to be encoded are developed. Furthermore, algorithms need to be developed that mimic the decision making process, which will in turn make use of these "subjective-free" descriptors. The ultimate process envisioned is one in which the analytical chemist can define the problem at hand by the utilization of several "key words" available to him, and subsequently match an analytical technique to suit his needs via an objective mathematical procedure.

The ensuing work has been performed to achieve two purposes. Primarily, it is intended to show that the techniques of pattern recognition have great practical significance in solving the problems of analytical chemistry. This will be illustrated by a novel application of pattern recognition to the discerning of the geographical origins of frozen concentrated orange juice via their trace element concentrations. Once the viability of the technique has been established, a discussion of its application to bringing together analytical problems and techniques will follow. The importance of establishing impartial and sensitive descriptors for the techniques will be emphasized, at which time the proposed descriptors will be introduced: selectivity, cost, time and linear dynamic range amongst others. Emphasis will be placed on making all proposed

figures of merit arithmetically quantifiable. Attempts will be made to calculate theoretical limits of detection for a variety of atomic spectroscopic techniques in order to establish means of comparing their ultimate capabilities. This in turn may find suitable usage in the pattern recognition problem as well.

CHAPTER ONE
PATTERN RECOGNITION

Introduction

The main purpose of pattern recognition is to categorize a sample of observed data as a member of a class to which it belongs. Typical examples of everyday usages of pattern recognition involve the evaluation of common objects such as Toyotas, German Shepherds and Professors as part of a larger class of automobiles, canines and humans. The actual mechanics of pattern recognition were not investigated until the 1950's with the advent of computers and the birth of cognitive psychology (1). Since then, pattern recognition has found many and varied applications which are dramatized by several excellent reviews which have appeared in the literature (2-6). The more notable applications of pattern recognition are the interpretation of printed characters (letters) and script (7), speech recognition, fingerprint analysis (8), analysis of microphotographs of biological material including blood cells and chromosomes (9), and the analysis of photographs of events in bubble, spark, or cloud chambers (10). With respect to chemical applications, pattern recognition has helped organize the enormous amount of complicated

spectra generated by such techniques as mass spectrometry and infrared spectrometry. It has helped elucidate structures of compounds when combining the information derived from both analysis.

Before discussing the present example of the application of pattern recognition, it would be instructive to acquaint the reader with the fundamental mathematical concepts and terminology. A simple physical interpretation will serve as a convenient starting point for our discussion. Essentially, we are interested in describing geometric regions in space and then finding a means to discriminate between them. The regions in space, or "categories," are described by "features," or "descriptors," of the measurement process. Each descriptor is associated with a vector whose direction defines a dimension, or axis of space, and whose magnitude defines the distance along that axis. For instance, if two elements (A,B) are to be analyzed quantitatively, in a particular sample matrix, we will be dealing with a 2-dimensional space whose magnitude along any axis is governed by the measured concentration for that element. We now can define a pattern vector for the results derived from one analysis of the two elements of interest as

$$X = (A,B). \qquad (1)$$

This vector now represents a single point in 2-dimensional space. If we now make the assumption that samples taken from a homogeneous population will display similar concentrations for the 2 test elements, then their associated pattern vectors will define points in a similar region in space.

We now have a basis upon which to form a category. Furthermore, with a second population, differing from the first with respect to the concentrations of the two target elements of interest, we can, by analogy, form a second category. Having formed these two categories, we are now able to distinguish between the two sample populations by merely distinguishing between the two categories formed in space. By examining Figure 1, it is apparent that a surface can be drawn that divides the two categories. This now transforms the question of "to what category does a point belong?" to "on which side of the dividing line does a point alleged to be in one of the categories fall?". This dividing line is appropriately termed a "decision vector"

$$D = (a,b) \tag{2}$$

for it allows us to make our final categorization decision. Upon obtaining the dot product of a pattern vector with a decision vector, the pattern vector is now fixed in space with respect to the decision vector. In the ideal case, the dot product of the decision vector and pattern vector will yield one of two results;

$$X \cdot D = \{Aa + Bb\} = S \tag{3}$$

where $S>0$ or $S<0$. Finally, we can arbitrarily define the decision vector such that when $S>0$, then X will belong to category I and when $S<0$, then X will belong to category II.

It should be pointed out at this time that rigorous mathematical procedures for both producing pattern vectors and decision vectors have been formulated (11-12). The

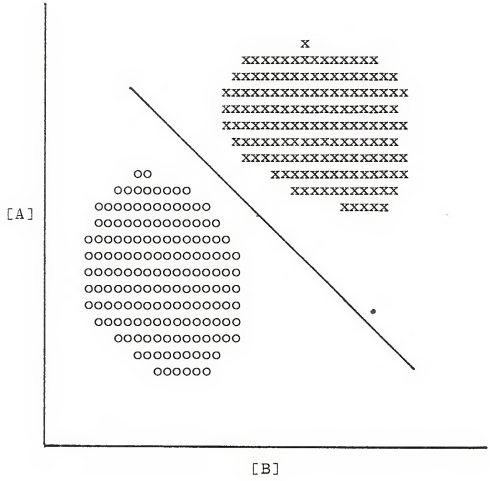

Figure I

Separation of Pattern Vectors
Derived from Two Distinctly Different Populations

programs developed allow patterns to be formed in data where upon inspection they are not readily apparent. This is extremely helpful in making otherwise intractable problems amenable to analysis by pattern recognition. However, for the less complex problems, upon careful examination of the data, an appropriate and effective decision vector can be arrived at with a minimal amount of effort. In the end, the efficiency of a decision vector is determined by repeated attempts at making the discriminating decision and recording the success rate.

Discrimination of Geographical Origins of Samples of Frozen Concentrated Orange Juice

Having covered the fundamentals of pattern recognition, we are ready to show its application to the present work. The objective of this study was to compare a number of samples of Florida and Brazilian orange juice concentrates as to their inorganic elemental content for the purpose of fingerprinting their geographical origins (13). A detailed sample preparation scheme has been formulated by McHard et al. (13) which essentially entails dry ashing 20 g samples of the frozen concentrated orange juice (FCOJ) for approximately 16 hours. Dissolution of the ash into 50 ml of 0.1 M HNO_3 is then followed by analysis by atomic emission spectroscopy. The instrument used was a Spectrametrics, Inc., Spectraspan II equipped with the Spectrajet III Plasma source. Details of the analysis can be found in McHard et al. (14),

while a compilation of their results can be found in Table I. From the results, McHard et al. were able to show that significant differences in concentrations existed between Floridian FCOJ's and Brazilian FCOJ's with respect to barium, boron, gallium, manganese and rubidium concentrations. It should be mentioned at this point that although concentrations in the FCOJ samples should ideally be analyzed with respect to a standard reference of known matrix composition, none was readily available for the analysis. Therefore, concentrations are reported as ratios to an internal reference element, zinc, which was shown to be of fairly constant concentration in both the Floridian and Brazilian populations. Furthermore, the use of a particular brand of Florida juice as a reference bypassed the need to account for solids content differences between the two populations. To lend statistical credence to the conclusions that fingerprinting elements had been established, an intensive statistical analysis of the data was performed. By use of Tschebycheff's inequality, numerical probabilities can be assigned to the chances of an analyzed sample being of Floridian origin. This entailed calculating means and standard deviations for the values of each of the elements found in the samples analyzed within the Florida population. This now became our reference population with which subsequent unknown analysis could be compared. We then assign a deviation 'α' for a test sample, which is a measure of the number of standard deviations away from the mean of the reference population that this value lies. From this a probability (P) of the test sample being part of the Floridian

Table I

Results of the Analysis of Trace Metals in
Floridian and Brazilian Sample of FCOJ

Element	λ(nm)	Florida Conc.Range PPM	Brazil Conc.Range PPM	Florida[a] Ratio Range	Brazil[a] Ratio Range
Al	396.153	0.045-0.125	0.070-10.0	0.8275-2.2412	0.7210-8.5565
[b]As	234.984	<.05			
Ba	455.404	0.025-0.070	0.185-0.750	0.7833-2.9661	5.150-24.8913
[b]Be	234.861	<0.05			
[b]Bi	306.716	<0.05			
B	249.773	0.950-1.20	0.900-2.15	0.5938-0.8702	0.9448-1.6979
Ca	422.673	65-100	80-120	0.6082-0.8512	0.7812-1.4030
Cr	425.435	0.002-0.020	0.002-0.065	0.3079-1.5597	0.4470-6.9348
[b]Co	345.351	<0.01			
Cu	324.754	0.350-0.425	0.200-0.400	0.6254-0.9410	0.6430-1.1205
Ga	403.298	0.030-0.040	0.063-0.145	0.9403-1.2812	1.3794-3.1828
In	451.132	0.001-0.002	0-0.013	0.2348-0.7147	0-1.9425
Fe	358.120	0.800-6.90	0.975-17.5	0.4118-3.3753	0.6190-7.3848
La	394.911	0.003-0.020	0.0.048	0.1529-1.1799	0-1.6886
Pb	405.782	<0.15			
Li	670.781	0.001-0.002	0.002-0.005	0.3064-0.6299	0.5600-21.4273

continued

Table I-continued

Element	λ(nm)	Florida Conc.Range PPM	Brazil Conc.Range PPM	Florida[a] Ratio Range	Brazil[a] Ratio Range
Mg	285.213	95-120	130-170	0.7952-1.0045	0.2807-1.4743
Mn	403.307	0.250-0.315	0.450-0.800	0.8597-1.0586	1.3916-3.2465
Mo	379.825	0-0.003	0-0.005	0-2.1460	0-3.8231
Ni	341.477	0.010-0.025	0.008-0.090	0.4085-1.4741	0.3676-1.3867
P	214.911	120-155	155-310	0.6740-1.0620	0.0540-1.5971
K	766.491	1500-1650	2030-2400	0.7395-1.9768	0.8870-1.5288
Rb	780.023	0.365-0.740	2.65-6.48	0.6928-1.8473	6.0511-11.4510
Sc	361.384	0-0.001	0-0.003	0.0236-0.2203	0.0104-5.9318
Ag	328.068	<0.001	0.001-0.035		0.0980-1.5819
Na	588.995	1.85-4.30	1.50-25.5	0.4253-1.0128	0.0453-7.0694
Sr	460.733	0.095-0.980	0.290-1.10	0.1992-1.6705	0.2652-2.0183
Sn	303.412	0-0.420	0.015-2.58	0-2.5987	0.3304-52.1195
Ti	334.941	0.005-0.020	0.015-0.350	0.4370-1.4601	0.7815-28.7269
V[b]	437.924	0.01			
Y[b]	412.831	<0.1			
Zn	213.856	0.350-0.450	0.250-0.425		

a - ratios of concentrations as described in McHard et al. (13)

b - concentration below detection limit

population can be calculated using Tschebycheff's inequality,

$$P(|\bar{x} - x|) > \alpha s = \frac{1}{\alpha^2} \quad . \tag{4}$$

This method is quite successful at achieving its intended goal of discriminating between the two populations. However, regardless of its intuitive appeal due to its simplicity, the calculations needed to arrive at a decision are tedious and time consuming at the very best. What is proposed is the utilization of a somewhat less common mode of analysis of the data which also has great discriminatory power, yet entails a much less laborious manipulation of the data. The advantages of the application of pattern recognition techniques to this problem over those of the traditional statistical methods will be discussed in greater detail after the problem has been worked out.

The same five elements chosen by McHard et al., i.e. barium, boron, gallium, manganese and rubidium, are the ones chosen for this analysis. This was done to allow a direct comparison between the two methods. In actuality, further optimization of the pattern recognition technique can be realized if the remaining 21 elements were objectively tested (11) to determine their suitability as discriminating descriptors. However, upon inspection of the data base of these 5 elements, it is seen that they exhibit no, or minimal, overlap in their ranges which does indeed allow for precise category formation. We were also fortunate enough to have the absolute values of the ranges of concentrations to be approximately equal (see Table II). If this were not so, we

Table II

Summary of Concentration Ranges for the Five Fingerprinting Elements in Brazilian and Floridian Samples of Frozen Concentrated Orange Juice

	Fla.(ppm)[a]		Brazil(ppm)	
Ba	0.025-0.07	$\bar{x}$=0.048	0.139-0.53	$\bar{x}$=0.33
B	0.95-1.20	$\bar{x}$=1.08	0.675-1.61	$\bar{x}$=1.14
Ga	0.03-0.04	$\bar{x}$=0.035	0.047-0.11	$\bar{x}$=0.079
Mn	0.25-0.315	$\bar{x}$=0.28	0.30-0.60	$\bar{x}$=0.45
Rb	0.365-0.74	$\bar{x}$=0.55	1.98-4.86	$\bar{x}$=3.42

a - all values reported are adjusted for variations in solid content and express concentrations to be found in single strength orange juice

would perceive a disproportionate weighting factor assigned to that element whose concentration values were higher than the remaining ones. However, had the situation arisen we would have been able to linearize the data, thereby precluding this possibility (12).

Having chosen these 5 elements as our descriptors, we have established the fact that we will be forming categories in 5-dimensional space. Obviously, this problem cannot be handled graphically nor imagined by the human mind. This illustrates one of the main advantages of pattern recognition: the ability to handle multidimensional problems as easily as it handles those of lesser dimensions. As previously mentioned, the magnitude along any one particular axis is governed by the measured concentration for that particular element. We now can define a pattern vector for one sample set (one particular FCOJ sample)

$$X = ([Ba], [B], [Ga], [Mn], [Rb]) \quad (5)$$

This vector now represents a single point in 5-dimensional space that completely characterizes that one particular FCOJ sample. If we now make the assumption that similar FCOJ samples can be described by pattern vectors that define points in a similar region in space, we now have a basis upon which to form categories. The problem now reduces to one in which we are interested in discriminating between these categories. In practice, we are looking for a means whereby we can classify a sample into one of two categories, i.e., Brazilian FCOJ or Floridian FCOJ. The means by which this is accomplished is by the introduction of the

aforementioned decision vector. After careful inspection of the data in Table II, the following decision vector was arrived at:

$$D = (1, -1, -1, -1, 1) \quad (6)$$

The decision vector was formulated such that if the dot product of it and a sample vector (S) is less than zero, then X is a Floridian juice, and if S is greater than zero, then X is a Brazilian juice. The fact that the dot product would result in either a positive or negative integer is just a matter of convenience. Any arbitrarily chosen decision vector would be sufficient in defining the area in space that contains the categories of interest. Their boundaries, however, would not be as conveniently defined as in the present example. Nevertheless, once the boundaries are evaluated they can be utilized as equally effective vehicles of the decision making process.

In general, trace elemental concentrations in juices of Floridian origin were lower than those of non-domestic origin. Therefore, three cases were examined to detect the efficiency of the decision vector.

Case I. Here, we wish to distinguish between a Florida juice with the lowest possible values and a Brazil juice with the highest possible values.

Case II. Here, we wish to distinguish between a Florida juice with average values and a Brazil juice with average values.

Case III. Here, we wish to distinguish between a Florida juice with the highest possible values and a Brazil juice with the lowest values. Case III is the most important case because it represents the case where maximal overlap between the two origins may exist. The concentrations for any of the five target elements are assumed to be uncorrelated to one another. If this assumption is true, and experimental evidence indicates this, then the probability of finding a sample that has the concentrations of all five of the target elements stacked to one side of the mean is nominal. Therefore, case III actually represents the worst possible case we can ever expect to encounter and does not portray the average real sample. It is, however, the ultimate limiting case and will serve as a good indicator of pattern recognition's ability to discriminate between the two geographical origins. Referring to Table II, cases I-III will be evaluated:

Case I. a) X_1 = (0.025, 0.95, 0.03, 0.25, 0.37) (Floridian)

where the above vector represents the following ordering of elements:

(Ba, B, Ga, Mn, Rb)

and the decision vector was given by equation (6) as

$$D = (1, -1, -1, -1, 1).$$

We must evaluate the dot product of the two vectors, $D \cdot X_1$,

$$D \cdot X_1 = (0.025 - 0.95 - 0.03 - 0.25 + 0.37) = S$$

$$S = -0.84$$

$S<0$; therefore, X_1 is a Floridian juice.

b) X_2 = (0.53, 1.61, 0.11, 0.60, 4.86)
(Brazilian)

$D \cdot X_2 = 3.07$

$S>0$; therefore, X_2 is a Brazilian juice.

Case II. a) X_1 = (0.048, 1.08, 0.035, 0.28, 0.55)
(Floridian)

$D \cdot X_1 = -0.80$

$S<0$; therefore, X_1 is a Floridian juice.

b) X_2 = (0.33, 1.14, 0.079, 0.45, 3.42)
(Brazilian)

$D \cdot X_2 = 2.49$

$S>0$; therefore, X_2 is a Brazilian juice.

Case III. a) X_1 = (0.07, 1.20, 0.04, 0.315, 0.740)
(Floridian)

$D \cdot X_1 = -0.745$

$S<0$; therefore, X_1 is a Floridian juice.

b) X_2 = (0.139, 0.675, 0.047, 0.30, 1.98)
(Brazilian)

$D \cdot X_2 = 1.10$

$S>0$; therefore, X_2 is a Brazilian juice.

The results of the analysis of the five target elements were in actuality ratioed to zinc. To make the procedure functional for this set of data, the decision vector had to be modified to reflect the ratios as tabulated in Table I. The new decision vector is

$$D_n = (1, -2, -2, -2, 1).$$

We will now repeat case III to substantiate the efficiency

of the new decision vector.

Case III. a) X_1 = (2.9661, 0.8702, 1.2812, 1.0586, 1.8473)
(Floridian)

$D_n \cdot X_1 = -1.603$

$S<0$; therefore, X_1 is a Floridian juice.

b) X_2 = (5.150, 0.9448, 1.3794, 1.3816, 6.0511)
(Brazilian)

$D_n \cdot X_2 = 3.789$

$S>0$; therefore, X_2 is a Brazilian juice.

Conclusion

It has been shown that for the worst possible case in which all elements of interest in a Florida FCOJ have their highest possible values, and those of the Brazilian FCOJ have their lowest, the proposed technique offers a clear and substantial separation of the two groups. With the sample of the population that has been obtained to date, the decision vector is 100% successful. Furthermore, after having recognized that patterns were being formed by the data, the application of pattern recognition techniques to the problem proved trivial. This is a point which the author wishes to emphasize. Although it is recognized that pattern recognition can handle problems that otherwise are too complex, it also is a viable technique to use when conventional statistical and probabilistic methods can ordinarily be used. The distinct advantage comes from the time saving aspect of the minimized number of calculation

steps needed in order to arrive at a decision. Once the data base is established and a proper decision vector is formed, the actual testing of the data becomes very rapid. It is the author's opinion that this alone makes the pattern recognition technique attractive. There is one other advantage that may not be so apparent and should be pointed out. This lies in the fact that once a person is exposed to the techniques of pattern recognition, he begins to cognizantly think in terms of groups or patterns. This allows interrelationships between items to be scrutinized from a natural perspective, i.e. in terms of patterns. Once exposed to the techniques of pattern recognition, and after familiarizing oneself with the basic mathematical tools of the technique, more and more problems will become amenable to being tackled by pattern recognition. Pattern recognition is a powerful mathematical technique that allows strong conclusions to be drawn about sets of data with great confidence. It may not replace more traditional statistical methods, but can definitely serve as an attractive alternative.

CHAPTER TWO
METHOD COMPARISON

Introduction

As was stated in the introduction, one of the major goals of this work is to show the applicability of pattern recognition techniques to the problem of choosing between a variety of analytical tecniques to solve a specific analytical problem. Many authors have addressed themselves to the problem of objective method comparison and a variety of approaches have been developed.

One of the simplest and most straightforward approaches to method comparison was first presented by McFarren et al. (15). Their approach was based on the assumption that the only criterion of interest to an analyst about to chose between several analytical techniques to solve a particular problem is its error content. A proposed "total error" of an analytical technique is calculated and criterion by which decisions will be made based on the total error calculations is established. The formula for calculating the total error of an analytical technique is

$$\frac{|E_m| + 2(s)}{X_t} \times 100 = \text{Total error} \qquad (1)$$

where

E_m = absolute value of mean error

s = standard deviation of the measurements

X_t = true value of the analyzed component.

The mean error is defined as the difference between the average of a series of test results and the true result. The standard deviation retains its classical definition which can be found in any elementary statistics book.

Upon calculation of the total error, which is actually a measure of the precision plus accuracy of the technique, it remains to be compared to the accepted evaluation criterion and a decision is then made. The proposed criterion was that any technique that exhibited a total error of less than 25% was judged to be excellent. Those techniques with a total error greater than 25% but less than 50% were judged to be acceptable while those having total errors greater than 50% were judged unacceptable. In order to make this approach viable, certain variables have to be strictly defined. For instance, methodologies for sample analysis have to be optimized and explicitly recorded. This is true under any and all circumstances if meaningful comparisons are to be made. Instruments must be carefully calibrated, reference standards must be established and proper blank correction must be performed. There are several major drawbacks to this approach which should be pointed out. Primarily, the total error of analysis may not be the sole determining factor of the applicability of an analytical technique. The cost of the analysis is always a major consideration when faced with

various budgetary constraints. Can the same information, or at least information that will still suit the needs of the analyst, be obtained at a lower cost? Another factor that must be considered is the speed of the analysis. It would be foolish to choose a particular analytical method that required time consuming preparative steps when a direct analysis can be done (assuming all other variables remain constant). What all this is leading to is that, when faced with making the type of decision we are discussing here, all pertinent figures of merit for the proposed analytical techniques must be looked at. It is insufficient to just consider the precision and accuracy obtainable by any particular analytical method. One of the first scientists to identify the need to establish good qualitative figures of merit which are quantifiable was Heinrich Kaiser (16). It was his goal to reduce the task of choosing between analytical methods to a purely mathematical process. Using the ideas and terminology of pattern recognition, one would have to represent the different possible analytical problems as points in a multi-dimensional space. With this designation, related problems would inevitably become neighboring points in this space. Furthermore, a corresponding order must be given to the various analytical procedures, which can be represented as points in the space of procedures. The problem now becomes reduced to one of establishing a correlation between points, or regions, in the two spaces. Or, if both procedures and problems are defined by the same descriptor, and we are interested in determining what procedure to use for a particular problem, the problem is reduced to one

of determining the appropriate category to which the problem descriptors belong. This is analagous to the problem of deciding upon the geographical origins of a particular frozen concentrated orange juice sample which was discussed previously.

As with any pattern recognition problem, the effectiveness of its application is solely determined by the chosen descriptors. They must be good indicators of the techniques and should, ideally, be independent of one another. A more fundamental necessary condition for any effective descriptor is its ability to be assigned discrete numerical values. It should be fairly apparent that when trying to associate a particular analytical method with a specific problem, it is important to know the limit of detection of the techinique, its linear dynamic range, its selectivity and specificity, the approximate speed and cost involved, the sample size needed and its allowable physical and chemical form, the accuracy and precision that is obtainable, as well as whether or not the instrument is available to the analyst. All of these figures of merit seem intuitively appropriate to the method comparison problem; however, it is not readily apparent how to quantify some of them.

To date, only one attempt has been made to actually apply the techniques of pattern recognition to the problem of deciding amongst a variety of analytical techniques to solve a particular analytical problem (17). This work concerned itself with discriminating between the applicability of UV-Vis Molecular Absorption Spectrophotometry (MA) and

Atomic Absorption (AA) Spectrophotometry to specific analytical problems. The author defined several descriptors and was able to assign quantitative ranges for their values. The questions Dr. Vandeginste asked whose answers defined the descriptors used are as follows:

a) Is the analysis for qualitative or quantitative work?
b) What is the accuracy?
c) What is the cost of the analysis?
d) What is the analysis time?
e) Is the analysis destructive or nondestructive?
f) What is the sample quantity needed for analysis?
g) What is the concentration to be determined?
h) What is the compound?
i) What type of matrix is it in?

After surveying the literature for problems that have already been solved by either MA or AA, a total of 237 articles were chosen. Of these 237, 157 were chosen to produce the methodology space. The remaining 80 papers were to be used as the problem vectors and were to be categorized with respect to the two categories formed in methodology space. The results of this approach were surprisingly good considering the fact that the chosen figures of merit are not necessarily the optimal ones to be used. Correct classifications were made on the order of 85% of the time. The major obstacle to Dr. Vandeginste's work, as well as to that of any researcher in the field, is the lack of proper documentation found in the literature. For instance, although the cost of an analysis would seem to be a figure of merit when

comparing analytical methodologies, very few authors choose to report the dollar and cents figures involved with their analysis. Furthermore, the time of an analysis seems as if it should be a crucial deciding factor when chosing amongst analytical techniques, yet, it too is seldom reported in the literature. The only categorical exception to this is the reporting of elution times in chromatographic analyses. However, even in chromatographic methods, elution times may not be the sole determinants of the total analysis time. There may be various steps in sample pretreatment which may or may not be the rate determining steps with respect to the entire analytical procedure. The omission of these and other figures of merit from the literature is not a mere oversight of the respective authors. More precisely, it appears as if the need to report these figures of merit has not been established. This perhaps stems from the lack of a clear and concise format for reporting them. To illustrate some of the difficulties involved with precisely defining a figure of merit and assigning it a numerical value, let us look at a few examples.

Figures of Merit

Time of Analysis

If a particular laboratory worker is interested in adopting a new analytical method to analyze for a particular sample and is particularly interested in minimizing the time of analysis, assuming all other figures of merit remain equal, how should he go about doing this? To begin with, before actually performing the analysis a technician will have

to be trained on the particular instrument involved. The time taken to accomplish this may vary drastically depending on the experience of the analyst and the complexity of the analysis. This is an important consideration with respect to the total analysis time but will not be quantified due to its great variability. Assuming that adequate training has been provided we now can take a closer look at the actual analysis time involved. It should be kept in mind that we are hoping to achieve a maximum amount of uniformity and the ability to define precisely the total analysis time such that interlaboratory comparisons could be monitored objectively. In the following discusssion, we will be considering the analysis of a sample by instrumental means only; however, a more general approach can be realized to encompass any mode of analysis.

Standard and reagent preparation. If we designate the total amount of time needed to prepare stock solutions of standards and necessary reagents as (t), and the number of analysis that these stock solutions will last for as (n), then we can define the total time needed to prepare all necessary solutions per analysis as

$$t_r = t/n \qquad \text{(minutes/analysis)}$$

Pretreatment. Any time necessary to pretreat the sample and make it amenable for analysis must be considered. We will designate this time interval as (t_p) and will include the time needed for any physical or chemical treatments of the samples as needed.

Analysis. With respect to the instrument itself, we assume that suitable warmup to attain equilibrium can be achieved without operator attention. Therefore, the time required for analysis is defined as the time interval between the introduction of the first sample or standard into the instrument and the time it takes to receive adequate information from the instrument to allow calculation of the desired quantity. This time span can be designated by (t_a).

Calculation. Finally, once adequate information in the form of voltage measurements, digital readouts,etc., is obtained, the time needed to convert them into their final usable form is designated (t_c). If the instrument is interfaced with a computer this time span is nominal. However, in the case where it is not, this time interval may become significant.

To arrive at the total analysis time the four components are added algebraically,

$$t_{total} = t_r + t_p + t_a + t_c .$$

We now have a somewhat unperturbing method to calculate a total analysis time which then can be introduced into the pattern recognition problem. The effort involved to calculate the total time of analysis is minimal on the part of the analyst, yet, the results can prove very beneficial to method comparison studies. Hopefully, with explicit directions on how to go about performing these calculations,

cooperating researchers would make the effort to systemize the reporting of their results in the literature.

Cost of Analysis

Similarly, a systematic approach to calculating a total cost of analysis can be developed (18,19). The importance of this figure of merit can easily be appreciated and a straightfoward method for calculating a rough estimate would be welcomed. The major considerations are fourfold:

1 - cost of labor, C_l

2 - cost of instrument, C_i

3 - cost of instrument maintenance, C_m

4 - cost of supplies, C_s.

To estimate the cost of labor required to perform an analysis, one must simply consider the total analysis time (t_{total}) and multiply this value by the technician's hourly wages. The initial cost of the instrument should be available and after including the allowable depreciation due to wear and tear, the total yearly cost could be calculated if a finite expected lifetime is estimated. If records are available concerning the number of analyses performed per year then it is trivial to calculate the instrumental capital cost per analysis. With respect to the maintenance of the instrument, careful records should be kept detailing the number of service calls needed to keep the instrument in operating condition. If repairs are performed in house a logging of the man hours spent in repairs is necessary. Calculating the cost of maintenance per analysis requires

knowledge of the average cost spent on a yearly basis and dividing by the number of analyses performed during the same time period. This should include estimates of replacement parts as well. Estimating the amount of money spent on supplies may be a little more difficult than the preceding calculations. The majority of items used in an analysis such as glassware, chemicals, etc., need to be considered but could be included in general overhead incurred while running a laboratory. The only upkeep expenses that need be considered are the cost of specialty gases used, power consumption, etc. For the most part, the price for this aspect of the analysis with respect to the entire analytical procedure is negligible and will not be considered. Totaling the individual cost factors mentioned should give a reasonable estimate of the total cost of an analysis,

$$C_{total} = C_l + C_i + C_m + C_s.$$

In most cases if a specific task is to be accomplished the cost per analysis may be trivial with respect to the value of the information obtained (20). However, to treat the problem objectively, thereby enabling an unbiased decision to be arrived at concerning methodology choices, the cost per analysis should be included as a figure of merit. Depending on the relative emphasis placed on any one figure of merit being utilized in a pattern recognition problem, a relative weighting factor can be assigned (21), thereby stressing the most important criteria to be used and slighting those of lesser importance.

Linear Dynamic Range

Continuing on our quest to define appropriate figures of merit for analytical techniques, we now will consider the linear dynamic range associated with the response of the analytical method. Although it is obvious that knowledge of such a "performance characteristic" (22) would help define the extent of applicability of an analytical method, here too we are faced with a lack of precise definitions in the literature (23).

With respect to the upper limit of the concentration range, regardless of how it is defined it may usually be increased by (1) diluting the sample, (2) using a less sensitive response parameter (e.g., a less intense spectral line, etc.), or (3) altering the instrumental configuration (24). If any of the above are done to alter the upper limit of the concentration range than a new analytical method is produced by the strictest definition of "analytical method;"

> An analytical method is to be regarded as the set of written instructions completely defining the procedure to be adopted by the analyst in order to obtain the required analytical result (25).

Therefore, if these alterations are made they should be included in the description of the analytical method.

The upper limit of concentration can be defined in a variety of ways. For instance, it can be defined as that concentration which represents the point in the calibration curve immediately preceding a deviation from the theoretical relationship between concentration and intensity. This, however, would be inadequate in that linear calibration curves are not mandatory for performing quantitative analysis.

Another possible definition would be one that defined the upper limit of concentration to be the highest concentration used to prepare the calibration curve. This is somewhat of a better definition in that it specifies the limits to which the analytical technique has been tested, although there is a large amount of arbitrariness associated with picking the concentrations used. A more specific and useful definition would be one that chooses the upper limit of concentration as the greatest concentration for which quantitative tests of the precision and bias of analytical results have been made. This definition actually expresses the greatest concentration that has undergone experimental scrutiny and whose results for accuracy and precision are available for inspection. However, it must be stressed that although this definition appears to be the best one for the upper limit of concentration its value can easily be experimentally varied.

Conversely, a more invariable value for concentration is obtained when considering the lower limit of the concentration range. In this case, the limit of detection of the analytical technique is usually firm and can be improved only after considerable instrumental optimization. Although there seems to be general agreement as to how to define the detection limit of an analytical method today, it appears as if there has not always been a clear statistical definition available. Excellent review articles concerned with the historical development of the concepts behind defining a limit of detection have been presented by Kaiser (26, 27) and Currie (28). The accepted definition of the limit of

detection is (29) that concentration that would give a signal that is equivalent to three times the standard deviation of the blank measure. Algebraically this can be expressed as follows:

$$C_{lim} = 3(\sigma_{bl})\ (S)$$

where,

C_{lim} = concentration at detection limit

σ_{bl} = standard deviation of the blank

S = slope of the calibration curve.

Having defined the upper limit and lower limits of the concentration ranges that are produced by analytical methods, we now have a method for quantitating their values. These values can then be easily incorporated into the pattern recognition problem.

Selectivity

Another very important figure of merit for any analytical procedure is its degree of selectivity for the analyte of interest over any interfering constituent of the sample or blank matrix. In 1933, G. E. F. Lundell published an article in which the goals of the analytical chemist's work in terms of developing selective techniques were set forth,

> The determinator's salvation lies in the development of selective methods of analysis, and his final resting place will be a heaven in which he has a shelf containing 92 reagents, one for each element, where No. 13 is the infallible specific for Al, No. 26 the sure shot for Fe, No. 39 the unfailing relief for Y, and so on to U. (30).

Not only has Lundell's vision been made more inaccessible by the introduction of at least 13 more elements in the past

50 years, but his hopes have never come close to being realized. Nevertheless, his implication is that no analytical method should be judged acceptable unless a measure of its selectivity has been performed. Lundell goes on to say,

> There is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone. The rub comes in because elements never occur alone, for nature and man frown upon celibacy. Methods of determination must therefore be judged by their selectivity. It is in this respect that most methods are weak and improvements must come (30).

It is true that experimental improvements must be addressed to enhancing selectivity as well as limit of detectability; however, by what criterion does one judge selectivity? In the colloquial sense, the meaning of selectivity is obvious but how does one go about defining it quantitatively? In the areas of ion selective electrodes and ion chromatography, efforts have been made to define selectivity coefficients. However, no general approach to experimentally defining a selectivity for an analytical procedure has been developed. The theoretical groundwork defining selectivities has been formulated by Heinrich Kaiser (16); however, prior to this work, no experimental verification of its validity has been reported. If a numerical analysis of the selectivity of an analytical procedure can be developed an invaluable and sensitive figure of merit will result that can effectively be introduced into the pattern recognition problem. The following work has been undertaken with just such a purpose in mind.

An analytical procedure is said to be fully "selective" when it enables the different components in the sample to be

determined independently of each other. Therefore, the analyst using such a procedure can select which of the components are to be determined and which are not, without any risk or errors due to disregarding some components of minor interest. The phrase "more or less selective" indicates that selectivity is understood to be a metric quantity and Kaiser endeavoured to define it mathematically. This would enable numerical comparisons to be made of the varying degrees of selectivity of analytical techniques in general.

Theory

The numerical value of selectivity (Ξ) of a given analytical procedure can be derived from the system of calibration functions which represent the relationship between concentration (c) and measurable quantities (x) in a multicomponent analysis. A general derivation has been presented by Kaiser (31) but for the special case of trace elemental analysis, which we will consider here, a simpler method leads to the same results.

Consider a multicomponent system comprised of three components to be analyzed spectroscopically for their trace elemental content. If the elements exhibit no spectral overlap within the spectral bandpass of the monochromator and if no interelement matrix effects are present, then the analysis can be performed in a straightfoward manner. The analytical signals measured are functions of one component at any one particular wavelength and no deconvoluting of interferences has to be performed. However, if spectral

overlaps do exist, then the measured intensity is a function of all three components at any one wavelength. The contribution to the total signal by the analyte has to be determined before any quantitative information about the analyte can be obtained. Experimentally, this is done by measuring the intensity of the three component system at the three analytical wavelengths, thereby developing a series of three simultaneous equations called the calibration functions. These are represented as follows,

$$\begin{aligned} x_1 &= g_1(c_1, c_2, c_3) \\ x_2 &= g_2(c_1, c_2, c_3) \\ x_3 &= g_3(c_1, c_2, c_3) \end{aligned} \qquad (1)$$

The calibration function (g), is a function that relates the measured intensity (x) to the concentration of analyte (c) via the slope of the calibration curve. The contributions to the total measured intensity at any one wavelength from the various concentrations of matrix constituents, c_1, c_2, & c_3, are assumed to be independent of one another. Therefore, x_i is given as a linear combination of the intensities derived from the individual concentrations of sample constituents in a matrix consisting of n components. In general, for a multicomponent matrix with n components, the following set of equations can be derived expressing the signal intensity, x_i, monitored at any one wavelength,

$$\begin{aligned} x_1 &= \gamma_{11}c_1 + \gamma_{12}c_2 + \cdots\cdots + \gamma_{1n}c_n \\ x_2 &= \gamma_{21}c_1 + \gamma_{22}c_2 + \cdots\cdots + \gamma_{2n}c_n \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ x_n &= \gamma_{n1}c_1 + \gamma_{n2}c_2 + \cdots\cdots + \gamma_{nn}c_n \end{aligned} \qquad (2)$$

or,

$$x_i = \sum_{j=1}^{j=n} \gamma_{ij} c_j \qquad (3)$$

where $\gamma_{ij} = \frac{\partial x_i}{\partial c_j}$ is the slope (partial sensitivity) of the calibration curve when plotting x_i vs c_j (x_i is the signal for element i at wavelength λ_i and c_j is the concentration of the non-analyte species j). It should be emphasized that this equation is only applicable to the case in which each component (c_1, c_2, c_3, ...c_n) independently contributes to the signal at the analytical line (λ_i), and in which no multiplicative correlations appear amongst the sample components, i.e., no intercomponent effects like phosphorous on calcium (32) in flame spectrometry occur. Actually, expression (2) can be applied to atomic spectrometry only when the effects of concomitant species are limited to spectral interferences which are caused by overlapping atomic profiles (of emission or absorption) of the co-existing species at the wavelengths of the analytes.

From equation (2), a "calibration matrix" can be extracted and takes on the following form,

$$\begin{array}{l} \gamma_{11}, \gamma_{12}, \ldots\ldots\ldots, \gamma_{1n} \\ \gamma_{21}, \gamma_{22}, \ldots\ldots\ldots, \gamma_{2n} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \gamma_{n1}, \gamma_{n2}, \ldots\ldots\ldots, \gamma_{nn} \end{array} \qquad (4)$$

With the calibration matrix formulated, Kaiser has defined the selectivity, Ξ, as follows,

$$\Xi = \operatorname*{Min}_{i=1\ldots n} \frac{|\gamma_{ii}|}{\sum_{k=1}^{n} |\gamma_{ik}| - |\gamma_{ii}|} - 1 \qquad (5)$$

where $\underset{i=1...n}{\text{Min}}$ means that after evaluating the selectivity with respect to all of the components, i=1...n, the final value chosen to be the indicative selectivity of the technique is that value which represents the worst, or minimum, value. It is therefore assumed that the entire procedure's selectivity is limited by its worst individual measure of selectivity. Again, it should be stressed that Ξ is independant of the concentration of the species 'i' in the sample solution as well as any intercomponent effects.

In analytical spectrometry, particularly in atomic spectrometry, chemical and/or physical interferences (i.e., enhancement or depression in the production of analyte atoms or ions in the gaseous environment, such as flame, plasma, furnace, etc. (33)) are often more serious than spectral interferences. In this case, the selectivity of an analytical technique becomes concentration dependent upon the individual components in the sample. Therefore, a method for discerning the selectivity of an analytical technique when considering intercomponent effects as well as spectral interferences when either concentration dependent or independent needs to be developed. The following expression shows the relationship between the analytical signal measured and any spectral and intercomponent interferences,

$$x_i = \sum_{j=1}^{j=n} \gamma_{ij} c_j + \left(\sum_{j=1}^{j=n} \mu_{ij} c_j \right)_{c_i} \qquad (6)$$

where $\mu_{ij} = \left(\frac{\partial x_i}{\partial c_j}\right)_{c_i}$ is the slope of the calibration curve of x_i vs c_j but evaluated at the concentration of analyte species

(i) equal to c_i. Experimentally, μ_{ij} can be obtained by observing the dependence of signal x_i at analyte concentration c_i, on the concentration of interferent c_j, where the calibration solution also contains constant concentrations of other concomitant species (1, 2,....n) as well. In this case, it is obvious that all diagonal elements will by definition have a value of zero. Furthermore, equation (6) will revert back to equation (3) if no intercomponent effects occur.

In a similar manner to equation (2), expression (6) may be rewritten as follows,

$$\begin{aligned} x_1 &= \gamma_{11}c_1 + (\gamma_{12}+\mu_{12})c_2 + \ldots\ldots\ldots + (\gamma_{1n}+\mu_{1n})c_n \\ x_2 &= (\gamma_{21}+\mu_{21})c_1 + \gamma_{22}c_2 + \ldots\ldots\ldots + (\gamma_{2n}+\mu_{2n})c_n \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ x_n &= (\gamma_{n1}+\mu_{n1})c_1 + (\gamma_{n2}+\mu_{n2})c_2 + \ldots\ldots\ldots + \gamma_{nn}c_n. \end{aligned} \quad (7)$$

From equation (7), just as we did for the spectral interference case (refer to expressions (2)and(4)), a calibration matrix of the analytical procedure can be given as,

$$\begin{matrix} \gamma_{11} & (\gamma_{12}+\mu_{12}) & \ldots\ldots\ldots & (\gamma_{1n}+\mu_{1n}) \\ (\gamma_{21}+\mu_{21}) & \gamma_{22} & \ldots\ldots\ldots & (\gamma_{2n}+\mu_{2n}) \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots \\ (\gamma_{n1}+\mu_{n1}) & (\gamma_{n2}+\mu_{n2}) & \ldots\ldots\ldots & \gamma_{nn} \end{matrix} \quad (8)$$

Equation (8) is equivalent to the sum of the following two matrices which represent a spectral interference calibration matrix plus an intercomponent interference calibration matrix,

$$\begin{matrix} \gamma_{11} & \gamma_{12} & \ldots\ldots\ldots & \gamma_{1n} \\ \gamma_{21} & \gamma_{22} & \ldots\ldots\ldots & \gamma_{2n} \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots \\ \gamma_{n1} & \gamma_{n2} & \ldots\ldots\ldots & \gamma_{nn} \end{matrix} + \begin{matrix} 0 & \mu_{12} & \ldots\ldots\ldots & \mu_{1n} \\ \mu_{21} & 0 & \ldots\ldots\ldots & \mu_{2n} \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots \\ \mu_{n1} & \mu_{n2} & \ldots\ldots\ldots & 0 \end{matrix} \quad (9)$$

Having introduced the intercomponent interference into our calibration matrix, we are now in the position to refine Kaiser's definition of the selectivity of an analytical method to include these interferences as well as to introduce a concentration dependence upon these interferences. A concentration dependent total selectivity, Δ_c, which includes both the spectral and intercomponent interferences, as well as the effect of concentration on the signal levels, can be defined as

$$\Delta_c = \underset{i=1..n}{\text{Min}} \frac{|\gamma_{ii}|c_i}{\sum_{j=1}^{n} |\gamma_{ik} + \mu_{ij}|c_j - |\gamma_{ii}|c_i} - 1 \qquad (10)$$

Expression (10) accounts for the effect of component concentrations upon <u>both</u> spectral and intercomponent interferences. If intercomponent interferences are absent, then equation (10) becomes transformed to the following,

$$\Xi_c = \underset{i=1..n}{\text{Min}} \frac{|\gamma_{ii}|c_i}{\sum_{j=1}^{n} |\gamma_{ij}|c_j - |\gamma_{ii}|c_i} - 1 \qquad (11)$$

and if only the intercomponent interferences are present, then equation (10) reverts to

$$\xi_c = \underset{i=1..n}{\text{Min}} \frac{|\gamma_{ii}|c_1}{\sum_{j=1}^{n} |\mu_{ij}|c_j} - 1 \qquad (12)$$

Similarly, if the interferences, both spectral and intercomponent, are observed to be concentration independent then expressions (10) - (12) will take the form of the

following equations;

$$\Delta = \underset{i=1..n}{\text{Min}} \frac{|\gamma_{ii}|}{\sum_{j=1}^{n} |\gamma_{ij} + \mu_{ij}| - |\gamma_{ii}|} - 1 \qquad (13)$$

$$\Xi = \underset{i=1..n}{\text{Min}} \frac{|\gamma_{ii}|}{\sum_{j=1}^{n} |\gamma_{ij}| - |\gamma_{ii}|} - 1 \qquad (14)$$

$$\xi = \underset{i=1..n}{\text{Min}} \frac{|\gamma_{ii}|}{\sum_{j=1}^{n} |\mu_{ij}|} - 1 \qquad (15)$$

respectively.

In all cases, $\xi > \xi_c$, $\Delta > \Delta_c$, $\Xi > \Xi_c$. For example, when analyzing sea water, the high concentration of sodium appreciably interferes with the atomic absorption signals of several elements; in such a case, Ξ can be appreciable even though Ξ_c may indicate considerable spectral interferences. Finally, it should be stressed that for a completely selective analytical procedure, Ξ, Ξ_c, Δ, Δ_c, ξ and ξ_c are all infinite, whereas, for a completely non-selective procedure, the same parameters will all be -1. Any finite value less than infinity and greater than -1 will indicate an analytical procedure with some degree of selectivity.

Experimental

Materials. All reagents used were of reagent grade quality and standard stock solutions were prepared according to the procedure of Smith and Parsons (34). Dilutions of the

stock solutions were made covering the concentrations of elements as represented in Table III.

Instrumental. A Perkin-Elmer atomic absorption spectrophotometer (model 303) was used for the flame atomic absorption spectrometry studies. The air/acetylene flame (C_2H_2 flow rate: 3-6 l/min, air flow rate: 10 l/min) was ignited using a 10 cm slot burner. The experimental conditions, such as the burner position and fuel flow rate, were adjusted to obtain suitable signals. For the atomic emission plasma measurements, a SMI Spectrospan II emission spectrophotometer with a SMI Spectrojet III plasma excitation source was used. The detailed conditions of atomic emission observation were similar to references 13 and 14. The spectral bandpass for the atomic absorption and emission spectrometers were 6.8 Å and 0.1 Å respectively.

Procedure. The measured analytical lines of elements studied are listed in Table III. In most cases, the standard solution was not contaminated with the other elements (in the concentration range of interest) except for the following: zinc in potassium chloride, calcium carbonate and magnesium metal powder; manganese and iron in magnesium powder; and copper in potassium chloride and magnesium powder. The extents of these contaminations were estimated from emission spectrometry, namely, the estimated emission signals were monitored by scanning the echelle monochromator, and the observed emission signals were measured at just shorter and

Table III

Composition of Artificial Sea Water

Element	Concentration (ppm)	Wavelength (Å)
K	380	4044
Na	10,500	5890[a]
Mg	1,350	2796, 2852[b]
Ca	400	4228
Sr	8.0	4607
Cu	0.5[c]	3247
Zn	0.5[c]	2139
Fe	0.5[c]	2483, 3581[b]
Mn	0.5[c]	2794, 4033[b]
Cd	0.5[c]	2288

a - diluted 1,000 times

b - only for emission spectrometry

c - artificially added

Note: Concentrations express those of cationic species only.

longer wavelengths than the analyte wavelength. When no emission signals occured at these wavelengths, the emission at the analyte wavelength was assumed to be due to contamination, and so the results were corrected accordingly.

Results and Discussion

Spectral selectivity. Calibration matrices according to equation (4) have been obtained with respect to atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES) for a simulated sea water analysis. The calibration matrices for the sea water analysis are shown in Tables IV and V.

For AAS, major elements such as K, Na, Mg, and Ca produce spectral interferences at analytical lines of the other elements (at trace and lower concentrations). The main cause of these interferences seems to be the molecular absorption of these major elements such as the broad band absorption of sodium chloride in the UV region (35, 36, 37). The absorption of sodium chloride overlaps with the analytical lines of several trace elements (Fe, Zn, Cd). Although the partial selectivity (γ_{ij}) is much smaller than γ_{ii} of such trace elements, a spectral interference due to 10,000 ppm sodium can not be ignored in the determination of sub-ppm concentration of trace elements in the case of flame AAS (refer to Ξ_{ci} value in Table IV). Actually, Ξ_{ci} of AAS for sea water analysis is mainly limited by the interference of sodium on the iron absorption line.

Table IV

Calibration Matrix for Sea Water (Spectral Interference)
Analyzed by Atomic Absorption Spectrometry

Analyte \ Interferent	K	Na	Mg	Ca	Sr	Cu	Zn	Fe	Mn	Cd	Ξ_i	Ξ_{ci}
K	0.28	0	0.0020	0	0	0	0	0	0	0	140	39.0
Na	0	5.13	0	0	0	0	0	0	0	0	∞	∞
Mg	0.0047	0	0.042	0.0014	0	0	0	0	0	0	67.8	23.1
Ca	0	0	0	0.313	0	0	0	0	0	0	∞	∞
Sr	0	0	0	0	8.4	0	0	0	0	0	∞	∞
Cu	0	0.00040	0	0.0070	0	105	0	0	0	0	1.42 E+4	6.79
Zn	0	0.0016	0	0	0	0	170	0	0	0	1.06 E+5	4.31
Fe	0	0.00035	0	0.0090	0	0	0	55	0	0	5.88 E+3	2.94
Mn	0	0.00035	0.002	0.0013	0	0	0	0	154	0	4.22 E+3	10.5
Cd	0	0.00090	0.0035	0.0085	0	0	0	0	0	322	2.50 E+4	8.42

Table V

Calibration Matrix for Sea Water (Spectral Interference)
Analyzed by Atomic Emission Spectrometry

Analyte \ Interferent	K	Na	Mg	Ca	Sr	Cu	Zn	Fe	Mn	Cd	Ξ_i	Ξ_{ci}
K	1.70	0	0	0	0	0	0	0	0	0	∞	∞
Na	0	63	0	0	0	0	0	0	0	0	∞	∞
Mg	0	0	2.33	0	0	0	0	0	0	0	∞	∞
Ca	0	0	0	8.8	0	0	0	0	0	0	∞	∞
Sr	0	0	0	0	1660	0	0	0	0	0	∞	∞
Cu	0	0	0	0	0	9850	0	0	0	0	∞	∞
Zn	0	0	0	0	0	0	625	0	0	0	∞	∞
Fe	0	0.0011	0	0	0	0	0	733	0	0	6.66 E+5	32.3
Mn	0	-0.0016	0	0	0	0	0	0	2240	0	1.40 E+6	69.0
Cd	0	-0.0011	0	0	0	0	0	0	0	1480	1.35 E+6	66.3

Surprisingly, AES with the DC plasma-echelle monochromator system shows higher selectivity than AAS. For the manganese (4033 Å) and calcium (2288 Å) lines, 10,000 - 20,000 ppm sodium gave small negative signals. This interference might be interpreted as being indicative of a reduction of the background emission of the plasma due to the high concentration of sodium chloride. Small interferences due to the sodium chloride on Fe and Cd were observed.

The selectivities calculated from the calibration matricies are summarized in Table VI. The concentration independent selectivities (Ξ) are 30 - 10^5 times larger than the concentration dependent selectivities (Ξ_c), and selectivities for AES with a DC plasma-echelle monochromator system are 10 - 10^4 times larger than AAS. This can, in part, be attributed to the higher resolution of the spectrometer used in AES (approximately 10X higher) than the one used in AAS.

Intercomponent selectivity. The calibration matrix for intercomponent interferences in the sea water analysis by AAS is shown in Table VII. When determining the matrix, the blank solution, which includes all species except analyte, was used to obtain the base line in order to exclude spectral interferences and contamination.

The major interelement interference in the matrix is due to sodium chloride, which enhances potassium atomic absorption, whereas the addition of sodium chloride suppresses magnesium, calcium, and strontium atomic absorptions. The

Table VI

Selectivity Values for Sea Water Analysis

	Atomic Absorption Spectrometry	Atomic Emission Spectrometry
Ξ	67.8	6.66×10^5
Ξ_c	2.94	32.3
ξ	22.1	-
ξ_c	0.62	-

Table VII

Calibration Matrix for Sea Water (Intercomponent Interference)
Analyzed by Atomic Absorption Spectrometry

Analyte \ Interferent	K	Na	Mg	Ca	Sr	Cu	Zn	Fe	ξ_i	ξ_{ci}
K	-	0.0053	-0.0068	0	0	0	0	0	2.21 E+1	0.71
Na	0	-	0	0	0	0	0	0	∞	∞
Mg	0	-0.0035	-	0	0	0	0	0	1.20 E+2	0.62
Ca	0	-0.0014	-0.004	-	0	0	0	0	5.70 E+1	5.65
Sr	0	-0.0017	0	0	-	0	0	0	4.94 E+3	2.95
Cu	0	0	0	0	0	-	0	0	∞	∞
Zn	0	0	0	0	0	0	-	0	∞	∞
Fe	0	0	0	0	0	0	0	-	∞	∞

intercomponent selectivity factors (ξ_i and ξ_{ci}) for potassium (enhancement) and for magnesium (suppression) are both limited by sodium in sea water analysis. The calculated intercomponent selectivity values are shown in Table VII. It is clear that the intercomponent selectivity is much smaller than the spectral selectivity in the case of AAS.

Conclusion

More important than any specific conclusions that can be drawn from the examination of the results of these experiments is the fact that numerical values of selectivities are now made available. This capability now affords a very valuable figure of merit to be incorporated into the pattern recognition problem. In additon to all the other quantifiable figures or merit available such as cost of analysis, linear dynamic range (including limits of detection), sample size, sample type (binary classifiable (17)), accuracy, precision, etc., the selectivity should prove to be an effective descriptor for the pattern recognition problem. What remains to be done in the future is an inordinate amount of data collection and reduction before the marriage of an analytical problem and an appropriate technique can be realized from purely mathematical considerations.

CHAPTER THREE
THEORETICAL LIMITS OF DETECTION

Introduction

The groundwork established in the previous chapter is such that it can eventually succeed in bringing together any analytical problem with any available analytical technique. This capability would prove to be an extremely powerful diagnostic aid for the analytical chemist when faced with the task of solving difficult analytical problems. Another frequently encountered problem faced by the analytical researcher is one that concerns itself with the improvement of existing techniques such that they can be made amenable to the analysis of smaller and smaller quantities of analyte, i.e., improving detection limits. Some of the questions the analyst may ask while trying to achieve better detection limits are:

i. which parameters whould I try to vary?

ii. in which direction should the variation be made in order for me to realize an improvement in the detection limit?

iii. how much of an improvement can I expect in conjunction with a particular finite change in operating conditions?

iv. finally, at what point can I expect not to gain any more enhancement of detection limits, i.e., what is the theoretical limit of detection that can be attained under the best of conditions?

There are many empirical experimental approaches that can be utilized effectively to improve detection limits, although they make no effort to answer any of the aforementioned questions. From a practical viewpoint, these approaches are based solely on the operator's intuition and past experience, which may or may not be the most economical or efficient approach. If the analyst could be guided by theoretical considerations that could quickly expose the effects of altering instrumental parameters, a more objective approach to enhancing detection limits and understanding the inherent limitations of the techniques can be realized. Although this type of information can be extracted from the following theoretical calculations of limits of detection, this was not the intended purpose of this work. A comprehensive review of the application of signal-to-noise theory for these purposes can be found in Alkemade et al. (38) and Boutillier et al. (39). Primarily, the objective of this work was to make a comparison between the theoretical limits of detection of a variety of atomic plasma spectrometric techniques, and to assess the current "state of the art" with respect to realizing these limits. This will be accomplished by considering the major contributions and factors affecting both the signal production from the analyte, and limiting

noise sources associated with the measurement process. Furthermore, a theoretically calculated limit of detection may prove to be an important figure of merit to be used in the pattern recognition problem of Chapter Two. In effect, if no state of the art technique is available with sufficiently low detection limits, the analyst may choose to spend time optimizing if it is theoretically possible to achieve the appropriate sensitivity.

To be more specific, by means of signal-to-noise expressions for atomic absorption flame/plasma spectrometry (with narrow line and continuum sources), for atomic emission flame and ICP spectrometry, for atomic fluorescence flame spectrometry with "narrow" line conventional and high intensity (pulsed dye laser) sources, for atomic fluorescence flame spectrometry with "continuous" conventional and high intensity sources (pulsed and cw dye lasers), for photoacoustic spectroscopy with a cw high intensity source, and for optogalvanic spectroscopy with a pulsed high intensity source, detection limits (in atoms/cm^3 of gases) are estimated. In all cases, it is assumed that procedural errors are minimized, and that only noise sources in the instrumental methods are dominant. In particular, the limiting noises discussed are source transmitted shot noise, emission background shot noise and detector dark current shot noise; and emission background shot noise; for atomic absorption, atomic fluorescence and atomic emission spectrometry, respectively. For

the analysis of photoacoustic spectroscopy, Brownian motion of ambient air molecules is the limiting noise source, whereas shot noise due to the finite electron population in the flame is taken to be the limiting noise source for optogalvanic spectroscopy.

Conversion of the detection limits in terms of analyte atomic (ionic) species/cm^3 of hot gases to analyte solution concentration aspirated into the flame or plasma, will be performed. The expressions, and particularly the gaseous detection limits, are discussed in terms of the present "state of the art" of trace analysis, and with respect to expected improvements in detection limits as well. Also, the conversion to detection limits in liquid solution is discussed particularly with respect to the agreement between the predicted detection limits via the signal-to-noise ratio expressions, and the experimentally measured detection limits.

Explicit derivations of the signal and noise expressions will not be presented here, although, for in depth treatments, the reader is referred to the appropriate references as they are cited in the text. Furthermore, due to the natural division amongst the techniques that will be analyzed, i.e., those that use photomultiplier tubes as a detection device and those that do not (microphone and electrodes), the former techniques will be treated separately, holding off the analysis of photoacoustic spectroscopy and optogalvanic spectroscopy until the end.

The detection limit will be defined according to the IUPAC recommendation (29), i.e., the concentration resulting in a S/N = 3. For all atomic spectroscopic techniques, S/N expressions will be given in terms of digital integrated values (counts); all "intensities" will be given in terms of counts per second per x per y per z (x, y, z depend upon the type of intensity: an irradiance is in counts/s cm^2, a spectral irradiance is in counts/s cm^2 nm, a radiance is in counts/s cm^2 sr, a spectral radiance is in counts/s cm^2 sr nm, etc.). The S/N expressions will be given so that the numerator is the complete signal expression and the denominator is the complete limiting noise expression.

In the following analysis, only atomic spectral techniques involving plasmas (flame, inductively coupled plasmas, etc.) will be considered. No attempt will be made to consider detection limits in furnaces, arcs and other devices where solid samples are measured. The reasons for this differentiation are i) the atomic plasma spectrometric methods all involve nebulizers and production of gaseous species in the plasma, ii) for solid sample devices, estimation of the concentration of analyte/cm^3 is of little interest, but rather the estimation of the absolute amount (in g) of the analyte to produce a certain species concentration is of greater interest, iii) solid sample devices produce a transient change in analyte species, and so both the integrated signal (over time) and the peak signal (at the time of maximum response) should be

calculated, iv) the noise sources in furnaces are not as well documented as flames and plasmas. In conclusion, due to the aforementioned points, there is no fair means of comparing furnace-arc atomic spectrometric systems with plasma atomic spectrometric systems, and so only the latter atomic systems will be considered here. We are now prepared to discuss the S/N expressions in more detail.

Analysis of Photomultiplier Techniques

Atomic Fluorescence Flame Spectrometry (AFFS)

It will be assumed here that the major (limiting) noise in AFFS is either detector shot noise (an ideal situation) or flame background emission shot noise, i.e., such noises as detector flicker noise, background emission flicker noise, source scatter shot and flicker noises, band (or line) concomitant fluorescence shot and flicker noises, band (or line) concomitant emission shot and flicker, and electronics noise are minimized either by modulation techniques, by physical separation of the concomitants, by more efficient atomization procedures, or by specialized methods such as ratioing techniques. The detector shot noise or the background emission shot noise are the remaining irreducible and limiting noises under these conditions.

Continuum source excitation (AFFSC)

The limiting detectable S/N for AFFSC assuming a low intensity continuum source, CL, is given by (40):

$$\left(S/N\right)^{AFFSCL}_{lim,\ DS} = \frac{10^7\, D_s\, \frac{\ell}{4\pi}\, \frac{\lambda_o^4}{8\pi c}\, E_{p\lambda}(\lambda_o)\, Y\, A_{ul}\, \frac{g_u}{g_l}\, n^L_T(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i}{(2\, D_D\, \tau_i\, \overline{R}_D\, \eta_E)^{\frac{1}{2}}}$$

assuming detector shot noise, DS, is limiting and by

$$\left(S/N\right)^{AFFSCL}_{lim,\ BS} = \frac{10^7\, D_s\, \frac{\ell}{4\pi}\, \frac{\lambda_o^4}{8\pi c}\, E_{p\lambda}(\lambda_o)\, Y\, A_{ul}\, \frac{g_u}{g_l}\, n^L_T(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i}{(2\, D_B\, B_{PB\lambda}(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)(\Delta\lambda_s)\tau_i)^{\frac{1}{2}}}$$

assuming background shot noise, BS, is limiting. All terms are defined below:

A_{ul} = transition probability (Einstein coefficient of spontaneous emission) for emission process, s^{-1}

ℓ = emission (fluorescence) path length, cm

λ_o = peak absorption wavelength, cm

Y = quantum efficiency of transition, dimensionless

g's = statistical weight of upper, u, and lower, l, levels, dimensionless

n^L_T = limiting detectable concentration of analyte in flame, cm^{-3}

Ω = spectrometer or entrance optics solid angle (whichever is limiting), sr

w,h = width, height of spectrometer slit (assumed to be limiting area), cm, cm

T_s = spectrometer/entrance optics overall transmission, dimensionless

D_s = duty factor for excitation/measurement of

fluorescence, dimensionless

D_D = duty factor for detector, dimensionless

$E_{P\lambda}(\lambda_o)$ = spectral photon energy at central absorption wavelength, $cm^{-2}\ s^{-1}\ nm^{-1}$

D_B = duty factor for measurement of background emission in flame, dimensionless

Q_D = photocathode quantum efficiency of photomultiplier detector, dimensionless

ε_D = first dynode efficiency of photomultiplier detector, dimensionless

η_E = efficiency of amplifier - discriminator - readout system, dimensionless

$\overline{R}_D$ = average dark current rate of detector, counts s^{-1}

$B_{PB\lambda}(\lambda_o)$= average flame emission background photon radiance, counts $s^{-1}\ cm^{-2}\ sr^{-1}\ nm^{-1}$

$\Delta\lambda_s$ = spectrometer bandpass, nm.

The limiting detectable S/N for AFFSC assuming a high intensity (CH) continuum source (i.e., one producing saturation) is given by,

$$\left(S/N\right)^{AFFSCH}_{lim,\ DS} = \frac{D_s \frac{\lambda}{4\pi} A_{ul} \left(\frac{g_u}{g_u+g_l}\right) n_T^L (\Omega w h T_s Q_D \varepsilon_D \eta_E)\tau_i}{(2\ D_D\ \tau_i\ \overline{R}_D\ \eta_E)^{\frac{1}{2}}}$$

assuming detector shot noise, DS, is limiting and by,

$$\left(S/N\right)^{AFFSCH}_{lim,\ BS} = \frac{D_s \frac{\lambda}{4\pi} A_{ul} \left(\frac{g_u}{g_u+g_l}\right) n_T^L (\Omega w h T_s Q_D \varepsilon_D \eta_E)\tau_i}{(2\ D_B\ \Delta\lambda_s\ \overline{E}_{PB\lambda}(\lambda_o)(\Omega w h T_s Q_D \varepsilon_D \eta_E)\tau_i)^{\frac{1}{2}}}$$

assuming background emission shot noise, BS, is limiting.

Line source excitation

The limiting detectable S/N for AFFSL assuming a low intensity narrow line source (LL), i.e., one with a line wdith, much narrower than the absorption line width is given by,

$$\left(S/N\right)^{AFFSLL}_{lim,\ DS} = \frac{10^7 D_s \frac{\ell}{4\pi} \frac{\lambda_o^4}{8\pi c} E_p(\lambda_o) Y A_{ul} \frac{g_u}{g_l} n \frac{L}{T} \frac{u}{\delta\lambda_D} (\Omega w h T_s Q_D \varepsilon_D \eta_E) \tau_i}{(2 D_D \tau_i \bar{R}_D \eta_E)^{\frac{1}{2}}}$$

assuming detector shot noise is limiting and by,

$$\left(S/N\right)^{AFFSLL}_{lim,\ BS} = \frac{10^7 D_s \frac{\ell}{4\pi} \frac{\lambda_o^4}{8\pi c} E_p(\lambda_o) Y A_{ul} \frac{g_u}{g_l} n \frac{L}{T} \frac{u}{\delta\lambda_D} (\Omega w h T_s Q_D \varepsilon_D \eta_E) \tau_i}{(2 D_B \bar{E}_{PB\lambda}(\lambda_o)(\Omega w h T_s Q_D \tau_D \eta_E) \Delta\lambda_s \tau_i)^{\frac{1}{2}}}$$

assuming background emission shot noise is limiting. All terms above have been previously defined except for,

$E_p(\lambda_o)$ = line source photon irradiance at the absorption line center, λ_o, photons s^{-1} cm^{-2}

u = profile factor (41) accounting for relative width of source line and absorption line and for their profiles, dimensionless

When using a high intensity (laser) narrow line source, two general cases can be considered, namely interaction of the laser line with a homogeneously broadened absorption line (collisional, Lorentzian broadening) and interaction of the laser line with a small group of absorbers having the proper translational (Doppler interval) energy which is the case of inhomogeneous broadening. The S/N expression for the

latter case is unique and is given below. The limiting detectable S/N for AFFSL assuming a high intensity line source, LH, is given by,

$$\left(S/N\right)^{\text{AFFSLH}}_{\text{lim, DS}} = \frac{D_s \frac{\ell}{4\pi} A_{ul} n_T^L \left(\frac{10^7 E_p(\lambda_o)\lambda_o^4}{16\pi c\, \delta\lambda_{eff}}\right)^{\frac{1}{2}} (\Omega w h T_s Q_D \varepsilon_D \eta_E)\tau_i}{(2D_D \tau_i \overline{E}_D \eta_E)^{\frac{1}{2}}}$$

assuming detector shot noise is limiting and by,

$$\left(S/N\right)^{\text{AFFSLH}}_{\text{lim, BS}} = \frac{D_s \frac{\ell}{4\pi} A_{ul} n_T^L \left(\frac{10^7 E_p(\lambda_o)\lambda_o^4}{16\pi c\, \delta\lambda_{eff}}\right)^{\frac{1}{2}} (\Omega w h T_s Q_D \varepsilon_D \eta_E)\tau_i}{(2D_B B_{p\beta\lambda}(\lambda_o)(\Omega w h T_s Q_D \varepsilon_D \eta_E)\Delta\lambda_s \tau_i)^{\frac{1}{2}}}$$

assuming background emission shot noise is limiting. All terms have been defined previously except for:

$\delta\lambda_{eff}$ = effective absorption linewidth = $\pi/2\ \delta\lambda_L$, nm

$\delta\lambda_L$ = Lorentzian absorption line width, nm

The preceeding expression for atomic fluorescence flame spectrometry are specifically meant to apply to the case where the typical atom considered is a two-level one undergoing a single photon excitation. However, two-photon processes are showing significant analytical utility (42,43) and hence will be considered here as well. The two processes of major importance are the two-photon absorption via a virtual intermediate level and that via a real intermediate level. For the case of the virtual level the S/N expression is given by the following:

$$\left(\frac{S}{N}\right)_{\substack{\text{lim, DS}}}^{\text{2 photon, virtual}} = \frac{\Delta\tau_L \frac{\ell}{4\pi} A_{ul} n_T^L E_{p\lambda}^2(\lambda_o)\delta\, Y(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i}{(2D_D\tau_i \bar{R}_D \eta_E)^{\frac{1}{2}}}$$

assuming the use of a low intensity continuum source of excitation and detector shot noise limitation. All terms have been previously defined except for δ = two photon absorptivity ($cm^4 s$) and $\Delta\tau_L$ = pulse width of the laser (s). For the case in which a real intermediate level is used, the S/N expression is given by the following (assuming $g_u = g_\ell$),

$$\left(\frac{S}{N}\right)_{\substack{\text{lim, DS}}}^{\text{2 photon, real}} = \frac{D_s \frac{\ell}{4\pi} A_{ul} \frac{n_T^L}{4} (\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i}{(2D_D \tau_i \bar{R}_D \eta_E)^{\frac{1}{2}}}$$

where all terms have been previously defined and assuming a high intensity continuum source of excitation that produces saturation of both of the two photon transitions.

Atomic Emission Plasma Spectrometry (AEPS)

In this case, the plasma can be a dc plasma, an inductively coupled plasma, a capacitively coupled microwave plasma, a flame, etc. The major noise source will be assumed to be background emission shot noise, although in reality background flicker noise or emission shot noise or flicker noises due to concomitants may be the major noise source.

Assuming the background shot noise limitation, the limiting S/N expression is given by the following,

$$\left(S/N\right)_{\text{lim, BS}}^{\text{AEPS}} = \frac{10^7 \, \ell \, \frac{\lambda_o^4}{8\pi c} \frac{g_u}{g_l} A_{ul} \, n_T^L \, \overline{B}_{P\lambda}^{bb}(\lambda_o)(\Omega w h T_s Q_D \varepsilon_D \eta_E)\tau_i}{(2\overline{B}_{PB\lambda}(\lambda_o)(\Omega w h T_s Q_D \varepsilon_D \eta_E)\Delta\lambda_s \, \tau_i}$$

where all terms have been defined previously except for the following,

$\overline{B}_{PB\lambda}(\lambda_o)$ = average photon spectral radiance of plasma background evaluated at the analyte line center, photons s^{-1} cm^{-2} nm^{-1} sr^{-1}

$\overline{B}_{P\lambda}^{bb}(\lambda_o)$ = average photon spectral radiance of a blackbody radiator evaluated at the analyte line center and at the plasma temperature, photons s^{-1} cm^{-2} nm^{-1} sr^{-1}

ℓ = emission pathlength, cm.

Atomic Absorption Flame Spectrometry (AAFS)

In atomic absorption flame spectrometry, the major noise sources are associated with source transmitted shot and flicker noise and flame background emission shot noise. Other noise sources can generally be minimzed by various types of modulation techniques or are negligible compared to the above major noise sources. In this analysis, we will assume the major noise source is source transmitted shot noise, SS.

Continuum source excitation (AFFSC)

In this case, the limiting S/N expression is given by the following equation,

$$\left(S/N\right)_{\substack{\text{lim, SS}}}^{\text{AAFSC}} = \frac{10^7 D_s \ell \frac{\lambda_o^4}{8\pi c} \frac{g_u}{g_l} A_{ul} n_T^L B_{PC\lambda}(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i}{(2D_s B_{PC\lambda}(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)\Delta\lambda_s \tau_i)^{\frac{1}{2}}}$$

Line source excitation (AAFSL)

For the case of line source excitation the S/N expression is given by,

$$\left(S/N\right)_{\substack{\text{lim, SS}}}^{\text{AAFSL}} = \frac{10^7 D_s \ell \frac{\lambda_o^4}{8\pi c} \frac{g_u}{g_l} A_{ul} n_T^L(\frac{u}{\delta\lambda_D}) B_{PL}(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i}{(2D_s B_{PL}(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i)^{\frac{1}{2}}}$$

where all terms except those below have been previously defined,

B_{PL} = photon radiance of line source evaluated at analyte line center, photons s^{-1} cm^{-2} sr^{-1}

Evaluation of Other Noise Sources

In the above cases only specific noise sources for each method were considered and the specific noises (in counts) were given in the denominator of each expression. In this section, several other noise expressions (in counts) are given and can be substituted in the denominator for the specific case if one wishes to obtain $(S/N)_{lim}$ for other limiting cases than those given previously.

Plasma (flame) background flicker noise

$$N_{FBF} = (2)^{\frac{1}{2}} \xi_B \bar{B}_{PB\lambda}(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)\Delta\lambda_s \tau_i$$

where ξ_B = flicker factor for background emission as explained in Appendix B, dimensionless

Continuum source flicker noise in AA

$$N_{CF} = (2)^{\frac{1}{2}} \xi_C B_{PC\lambda}(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)(\Delta\lambda_s) \tau_i$$

where ξ_C = flicker factor for continuum source, dimensionless

Line source flicker noise in AA

$$N_{LF} = (2)^{\frac{1}{2}} \xi_L B_L(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i$$

where ξ_L = line source flicker factor, dimensionless

Continuum source scatter flicker noise in AF

$$N_{SCF} = (2)^{\frac{1}{2}} \xi_{SC} \left(\frac{d\sigma_S}{d\Omega}\right) n_S \ell E_{PSC}(\lambda_o)(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i$$

where $\frac{d\sigma_S}{d\Omega}$ = differential cross-section for scatter, $cm^2\ sr^{-1}$

ξ_{SC} = continuum source flicker factor, dimensionless

n_S = concentration of scattering species, cm^{-3}

$E_{PSC}(\lambda_o)$ = spectral source (continuum) irradiance at λ_o, photons $s^{-1}\ cm^{-2}\ nm^{-1}$

ℓ = pathlength of scatter in direction of detector, cm

Line source scatter flicker noise in AF

$$N_{SLF} = (2)^{\frac{1}{2}} \xi_{SL} E_{PL}(\lambda_o) \left(\frac{d\sigma_S}{d\Omega}\right) n_S \ell(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i$$

where ξ_{SL} = line source scatter flicker factor, dimensionless

$E_{PL}(\lambda_o)$ = line source photon irradiance at λ_o, photons s^{-1} cm^{-2}

Continuum source scatter shot noise in AFS

$$N_{SCS} = (2E_{PSC}\left(\frac{d\sigma_S}{d\Omega}\right) n_S \ell(\Omega whT_s Q_D \varepsilon_D \eta_E)\Delta\lambda_s \tau_i)^{\frac{1}{2}}$$

Line source scatter shot noise in AFS

$$N_{SLS} = (2E_{PL}\left(\frac{d\sigma_S}{d\Omega}\right) n_S \ell(\Omega whT_s Q_D \varepsilon_D \eta_E)\tau_i)^{\frac{1}{2}}$$

No expressions will be given for concomitant band or line fluorescence, emission flicker or shot noise, because these noise sources are very specific (to certain wavelength regions) and so can be avoided either by separation in a spectral region free of concomitant fluorescence or the concomitant can be physically separated and thus be made negligible. Finally, no noise expressions will be given for multiplicative noises, such as variation in aspiration flow rate, droplet dispersion rate, desolvation variations, and vaporization changes because they can be minimized by either instrumental improvements and/or by the use of internal standards or ratioing methods.

Results

The results of the calculations of theoretical detection limits for various plasma spectrometric techniques, employing photomultiplier tubes as the detection device, can be found in Tables VIII and IX. The parameters used to estimate the detection limits are listed in Table X. The values of the parameters were chosen in the following manner:

i) for all cases, a highly probable transition (high A_{ul}) was chosen;

ii) for all cases, a short (300 nm) and a long (600 nm) line was chosen to indicate the effect of wavelength;

iii) for all atomic fluorescence calculations, realistic estimates of quantum efficiencies were made for the flames/plasmas of interest;

iv) flame background spectral radiance estimates were based upon the results of Gilbert (44) and Fujiwara et al. (45). ICP plasma background spectral radiance estimates were based upon emissivity estimates from Dresvin (46) and temperature measurements by Eckert (47);

v) Doppler half widths were calculated (48) assuming an atom of 50 amu and the temperature of the flame or plasma; the Lorentzian half width was estimated from the work of Wagenaar (49); the effective lifetime, τ, was estimated from Lijnse (50);

vi) blackbody spectral radiances came from Planck's radiation distribution law as listed by Pivansky and Nagel (51);

Table VIII

Comparison of Calculated Detection Limits for Several Atomic Flame and Plasma Spectrometric Methods

Method / Cell	Limit of Detection(Atoms cm^{-3}, $\log_{10}$)			
	C_2H_2/Air	C_2H_2/N_2O	H_2/O_2/Ar	ICP
Atomic Fluorescence				
Xenon Arc Source (λ_o = 300 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2 s^{-1}$)	5.32	5.32	3.62	3.32
Detector Noise Limit ($\bar{R}_D = 10^4 s^{-1}$)	6.32	6.32	4.62	4.32
Background Noise Limit	8.76	9.26	7.06	7.26
Xenon Arc Source (λ_o = 600 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2 s^{-1}$)	3.11	3.11	1.41	1.11

continued

Table VIII-continued

Method / Cell	Limit of Detection (Atoms cm^{-3}, $\log_{10}$)			
	C_2H_2/Air	C_2H_2/N_2O	H_2/O_2/Ar	ICP
Detector Noise Limit ($\bar{R}_D = 10^4 s^{-1}$)	4.11	4.11	2.41	2.11
Background Noise Limit	5.70	6.20	3.00	5.20
Electrodeless Discharge Lamp (λ_o = 300 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2 s^{-1}$)	5.80	5.83	4.10	4.00
Detector Noise Limit ($\bar{R}_D = 10^4 s^{-1}$)	6.80	6.83	5.10	5.00
Background Noise Limit	9.23	9.76	7.54	7.94
Electrodeless Discharge Lamp (λ_o = 600 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2 s^{-1}$)	5.59	5.59	3.89	3.81
Detector Noise Limit ($\bar{R}_D = 10^4 s^{-1}$)	6.59	6.59	4.89	4.81
Background Noise Limit	8.18	8.68	4.88	7.90

continued

Table VIII-continued

Method / Cell	Limit of Detection(Atoms cm^{-3},log_{10})			
	C_2H_2/Air	C_2H_2/N_2O	$H_2/O_2/Ar$	ICP
*Band Dye Lasers, Normal (λ_o = 300 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2\ s^{-1}$)	4.20,2.12,3.12	4.20,2.12,3.12	2.50,0.42,1.42	2.20,0.12,1.12
Detector Noise Limit ($\bar{R}_D = 10^4\ s^{-1}$)	5.20,3.12,4.12	5.20,3.12,4.12	3.50,1.42,2.42	3.20,1.12,2.12
Background Noise Limit	6.63,5.56,6.56	7.13,6.06,7.06	4.93,3.86,4.86	5.13,4.06,5.06
*Band Dye Lasers, Normal (λ_o = 600 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2\ s^{-1}$)	1.99,-0.38,0.61	1.99,-0.38,0.61	0.29,-2.08,-1.09	-0.01,-2.38,-1.39
Detector Noise Limit ($\bar{R}_D = 10^4\ s^{-1}$)	2.99,0.62,1.61	2.99,0.62,1.61	1.29,-1.08,-0.09	0.99,-1.38,-0.39
Background Noise Limit	3.58,2.20,3.20	4.08,2.70,3.70	0.88,-0.50,0.50	3.08,1.70,2.70
*Band Dye Lasers, Saturation (λ_o= 300 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2\ s^{-1}$)	-0.57,1.63,0.63	-0.57,1.63,0.63	-0.57,1.63,0.63	-0.57,1.63,0.63

continued

Table VIII-continued

Method / Cell	Limit of Detection (Atoms cm^{-3}, $\log_{10}$)			
	C_2H_2/Air	C_2H_2/N_2O	H_2/O_2/Ar	ICP
Detector Noise Limit ($\bar{R}_D = 10^4\ s^{-1}$)	0.43,2.63,1.63	0.43,2.63,1.63	0.43,2.63,1.63	0.43,2.63,1.63
Background Noise Limit	1.86,5.07,4.07	2.36,5.57,4.57	1.86,5.07,4.07	2.36,5.57,4.57
*Band Dye Lasers, Saturation (λ_o = 600 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2\ s^{-1}$)	-0.57,1.63,0.63	-0.57,1.63,0.63	-0.57,1.63,0.63	-0.57,1.63,0.63
Detector Noise Limit ($\bar{R}_D = 10^4\ s^{-1}$)	0.43,2.63,1.63	0.43,2.63,1.63	0.43,2.63,1.63	0.43,2.63,1.63
Background Noise Limit	1.01,4.22,3.22	1.52,4.72,3.72	0.02,3.22,2.22	2.51,5.72,4.72
Line Dye Lasers, Saturation (λ_o= 300 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2\ s^{-1}$)	0.46	0.46	0.46	0.46
Detector Noise Limit ($\bar{R}_D = 10^4\ s^{-1}$)	1.46	1.46	1.46	1.46
Background Noise Limit	3.90	4.40	3.90	4.40

continued

Table VIII-continued

Method / Cell	Limit of Detection (Atoms cm^{-3}, $\log_{10}$)			
	C_2H_2/Air	C_2H_2/N_2O	H_2/O_2/Ar	ICP
Line Dye Lasers, Saturation (λ_o = 600 nm)				
Detector Noise Limit ($\bar{R}_D = 10^2\ s^{-1}$)	-0.64	-0.64	-0.64	-0.64
Detector Noise Limit ($\bar{R}_D = 10^4\ s^{-1}$)	0.36	0.36	0.36	0.36
Background Noise Limit	1.95	2.45	0.95	3.45
Atomic Absorption				
Xenon Arc Source				
Source Shot Noise Limit (λ_o = 300 nm)	8.50	8.50	8.80	9.50
Source Shot Noise Limit (λ_o = 600 nm)	6.46	6.46	6.76	7.46
Hollow Cathode Discharge Lamp				
Source Shot Noise Limit (λ_o = 300 nm)	6.79	6.79	7.09	7.99
Source Shot Noise Limit (λ_o = 600 nm)	5.73	5.73	6.03	6.95

continued

Table VIII-continued

Method / Cell	Limit of Detection (Atoms cm^{-3}, log_{10})			
	C_2H_2/Air	C_2H_2/N_2O	H_2/O_2/Ar	ICP
Atomic Emission				
Background Shot Noise Limit (λ_o = 300 nm)	9.06	8.08	9.04	5.18
Background Shot Noise Limit (λ_o = 600 nm)	4.00	3.80	3.00	3.32

* - results are listed for the following, in order; CW Ar^+ pumped dye laser, N_2-pumped dye laser, flashlamp pumped dye laser

Table IX

Calculated Detection Limits for
Two Photon Excitation of
Atomic Fluorescence Flame Spectrometry

	Concentration (atoms/cm^3)
Virtual Level	
Detector Noise Limit ($R_D = 10^2\ s^{-1}$)	2.0×10^6
Detector Noise Limit ($R_D = 10^4\ s^{-1}$)	2.0×10^7
Real Level	
Detector Noise Limit ($R_D = 10^2\ s^{-1}$)	8.5
Detector Noise Limit ($R_D = 10^4\ s^{-1}$)	8.5×10^1

Table X

Evaluation of Parameters used to Calculate Detection Limits
(Species/cm^3)

Photon/Atom-Ion Characteristics

λ_o = 300 nm; $h\nu_o$ = 6.6×10^{-19} J

λ_o = 600 nm; $h\nu_o$ = 3.3×10^{-19} J

Y = 0.01 (atoms in C_2H_2 - based flames)

Y = 0.5 (atoms in $H_2/O_2/Ar$ flame)

Y = 1 (atoms/ions in ICP)

$g_u = g_l$; $A_{ul} = 10^8\ s^{-1}$ (for all atoms/ions assuming highly probable transitions)

$\delta\lambda_{eff}$ = 0.001 nm

$\delta\lambda_D(\lambda_o$ = 300 nm, M = 50 amu) = 0.0015 nm (T=2500 K)

$\delta\lambda_D(\lambda_o$ = 600 nm, M = 50 amu) = 0.003 nm (T-2500 K)

$\delta\lambda_D(\lambda_o$ = 300 nm, M = 50 amu) = 0.0016 nm (T=3000 K)

$\delta\lambda_D(\lambda_o$ = 600 nm, M = 50 amu) = 0.003 nm (T=3000 K)

$\delta\lambda_D(\lambda_o$ = 300 nm, M = 50 amu) = 0.0024 nm (T=6000 K)

$\delta\lambda_D(\lambda_o$ = 600 nm, M = 50 amu) = 0.005 nm (T=6000 K)

u = 0.5

Plasma/Flame Characteristics

C_2H_2/Air Flame: T=2500 K

$\bar{B}_{B\lambda}$ (300 nm) = 10^{-6} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$($1.5 \times 10^{12}$ photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}_{B\lambda}$ (600 nm) = 10^{-8} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$($3 \times 10^{10}$ photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

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continued

Table X-continued

C_2H_2/N_2O Flame: T=3000 K

$\bar{B}_{B\lambda}$ (300 nm) = 10^{-5} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$(1.5 x 10^{13} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}_{B\lambda}$ (600 nm) = 10^{-7} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$(3 x 10^{11} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$H_2/O_2/Ar$ Flame: T=2500 K

$\bar{B}_{B\lambda}$ (300 nm) = 10^{-6} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$(1.5 x 10^{12} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}_{B\lambda}$ (600 nm) = 10^{-10} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$(3. x 10^{8} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

ICP: T=6000 K, ε_λ = 10^{-5}(emissivity at λ_o = 300 nm and at 600 nm)

$\bar{B}_{B\lambda}$(300 nm) = 10^{-5} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$(1.5 x 10^{13} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}_{B\lambda}$(600 nm) = 10^{-5} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$(3. x 10^{13} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

Blackbody:

T=2500 K

$\bar{B}^{bb}_{\lambda}$(300 nm) = 2 x 10^{-5}J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$ (3. x 10^{13} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}^{bb}_{\lambda}$(600 nm) = 1 x 10^{-2} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$ (3. x 10^{16} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

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continued

Table X-continued

T=3000 K

$\bar{B}_{\lambda}^{bb}$(300 nm) = 6 x 10^{-4} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$

(9. x 10^{14} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}_{\lambda}^{bb}$(600 nm) = 5 x 10^{-2} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$

(1.5 x 10^{17} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

T=6000 K

$\bar{B}_{\lambda}^{bb}$(300 nm) = 1.5 x 10^{0} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$

(2. x 10^{18} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

$\bar{B}_{\lambda}^{bb}$(600 nm) = 3. x 10^{0} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$

(9 x 10^{18} photons $s^{-1}cm^{-2}sr^{-1}nm^{-1}$)

Cell Factors

Fluorescence (all flames and ICP):

l = 1 cm (EDL; xenon arc)

l = 0.5 cm (Dye lasers beam expanded)

Emission:

l = 2 cm (all flames)

l = 1 cm (ICP)

Absorption:

L = 10 cm (C_2H_2-based flames)

L = 5 cm (H_2/O_2/Ar flame)

L = 1 cm (ICP)

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continued

Table X-continued

Instrumental Measurement Factors

Fluorescence: $\Omega Wh\ T_s\ Q_D\ \varepsilon_D \eta_E = 5 \times 10^{-4} cm^2\ sr$;

$\Delta\lambda_s$ = 1 nm (all sources except cw dye laser)

$\Omega Wh\ T_s\ Q_D\ \varepsilon_D \eta_E = 5 \times 10^{-5} cm^2 sr$;

$\Delta\lambda_s$ = 0.1 nm (cw dye laser only)

η_E = 1 (in all cases)

Emission: $\Omega Wh\ T_s\ Q_D\ \varepsilon_D \eta_E = 1 \times 10^{-6} cm^2 sr$;

$\Delta\lambda_s$ = 0.01 nm (flame or ICP)

Absorption: $\Omega Wh\ T_s\ Q_D\ \varepsilon_D \eta_E = 5 \times 10^{-5} cm^2 sr$;

$\Delta\lambda_s$ = 0.1 nm (HCL)

$\Omega Wh\ T_s\ Q_D\ \varepsilon_D \eta_E = 1 \times 10^{-7} cm^2 sr$;

$\Delta\lambda_s$ = 0.01 nm (xenon arc source)

Integration Time, T_i = 10 s (all cases)

Modulation-Pulsing Conditions

Fluorescence: EDL or Xenon Arc Source:

$D_s = 0.5$, $D_B = D_D = 1$

Modulated CW Ar^+-Dye Laser:

$D_s = 0.5$, $D_B = D_D = 1$

Pulsed N_2-Dye Laser:

$D_s = D_B = D_D = 10^{-7}$

Pulsed flashlamp Pumped Dye Laser:

$D_s = D_B = D_D = 10^{-5}$

Emission: $D_s = D_B = D_D = 1$ (flames and ICP)

Absorption: $D_s = 0.5$ (all sources and all cell types)

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continued

Table X-continued

External Sources for AA/AF

HCL (u = 0.5):

$\bar{B}_L$ (300 nm) = 10^{-4} J $s^{-1}cm^{-2}sr^{-1}$
(1.5×10^{14} photons $s^{-1}cm^{-2}sr^{-1}$)

$\bar{B}_L$ (600 nm) = 10^{-4} J $s^{-1}cm^{-2}sr^{-1}$
(3×10^{14} photons $s^{-1}cm^{-2}sr^{-1}$)

Xenon Arc (300 W EIMAC Arc; $\Omega_{ex} \equiv 3\pi$ sr;
$E_{c\lambda} = \Omega_{ex} B_{c\lambda}$)

$\bar{B}_{c\lambda}$(300 nm) = 2×10^{-2} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$
(3×10^{16} photons $s^{-1}cm^{-2}sr^{-1}$)

$\bar{E}_{c\lambda}$(300 nm) = 2×10^{-1} J $s^{-1}cm^{-2}nm^{-1}$
(3×10^{17} photons $s^{-1}cm^{-2}$)

$\bar{B}_{c\lambda}$(600 nm) = 1×10^{-1} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$
(3×10^{17} photons $s^{-1}cm^{-2}sr^{-1}$)

$E_{c\lambda}$(600 nm) = 1×10^{0} J $s^{-1}cm^{-2}nm^{-1}$
(3×10^{18} photons $s^{-1}cm^{-2}$)

EDL (150 W; Ω_{ex} = 0.1 Sr; $\bar{E}_L = \Omega_{ex}\bar{B}_L$, u = 0.5)

$\bar{B}_L$ (300 nm) = 10^{-3} J $s^{-1}cm^{-2}Sr^{-1}$
(1.5×10^{15} photons $s^{-1}cm^{-2}sr^{-1}$)

$\bar{E}_L$ (300 nm) = 10^{-4} J $s^{-1}cm^{-2}$
(1.5×10^{14} photons $s^{-1}cm^{-2}$)

$\bar{B}_L$ (600 nm) = 10^{-4} J $s^{-1}cm^{-2}sr^{-1}$
(3×10^{14} photons $s^{-1}cm^{-2}sr^{-1}$)

$\bar{E}_L$ (600 nm) = 10^{-5} J $s^{-1}cm^{-2}sr^{-1}$
(3×10^{13} photons $s^{-1}cm^{-2}$)

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continued

Table X-continued

Dye Laser, CW Ar^+-Dye Laser, 1 W output at 600 nm, 0.05 W output at 300 nm, beam diameter before expansion ≅ 0.2 cm, beam diameter after expansion = 0.5 cm, band pass ∿0.01 nm, continuum source case).

$\bar{E}_{c\lambda}$ (300 nm) = 2.5×10^{1} J $s^{-1}cm^{-2}nm^{-1}$

(8×10^{19} photons $s^{-1}cm^{-2}nm^{-1}$)

$\bar{E}_{c\lambda}$ (600 nm) = 5×10^{2} J $s^{-1}cm^{-2}nm^{-1}$

(8×10^{20} photons $s^{-1}cm^{-2}nm^{-1}$)

Dye Laser, Pulsed N_2-Dye, 50 kW peak power, 5 ns pulses, 20 pps, beam diameter before expansion = 0.15 mm, beam diameter after beam expansion = 0.5 cm, band pass= 0.03 nm, doubling efficiency = 10% continuum source case)

$\bar{E}_{c\lambda}$ (300 nm) = 1×10^{6} J $s^{-1}cm^{-2}nm^{-1}$

(1.5×10^{24} photons $s^{-1}cm^{-2}nm^{-1}$)

$\bar{E}_{c\lambda}$ (600 nm) = 1×10^{7} J $s^{-1}cm^{-2}nm^{-1}$

(3×10^{25} photons $s^{-1}cm^{-2}nm^{-1}$)

Dye Laser, Pulsed N_2-Dye, same as above but with etalon narrowing, band pass is now 0.001 nm, narrow line source case)

$\bar{E}_{L}$ (300 nm) = 7×10^{3} J $s^{-1}cm^{-2}$

(1×10^{22} photons $s^{-1}cm^{-2}$)

$\bar{E}_{L}$ (600 nm) = 7×10^{4} J $s^{-1}cm^{-2}$

(1×10^{23} photons $s^{-1}cm^{-2}$)

Dye Laser, Flashlamp Pumped, 5 kW fundamental, 1 μs pulses, 10 pps, beam diameter before expansion ≃0.2 cm, beam diameter after expansion ≃0.5 cm, band pass = 0.1 nm doubling efficiency = 10% continuum source case)

$\bar{E}_{c\lambda}$ (300 nm) = 1×10^{4} J $s^{-1}cm^{-2}nm^{-1}$

(1.5×10^{22} photons $s^{-1}cm^{-2}nm^{-1}$)

Table X-continued

$\bar{E}_{c\lambda}$ (600 nm) = 1 x 10^{5} J $s^{-1}cm^{-2}nm^{-1}$

(3 x 10^{23} photons $s^{-1}cm^{-2}nm^{-1}$)

Saturation Conditions

Continuum Source

$\bar{E}_{c\lambda}^{*}$ (300 nm) > $\frac{6 \times 10^{4}}{Y}$ J $s^{-1}cm^{-2}nm^{-1}$

($\frac{9 \times 10^{22}}{Y}$ photons $s^{-1}cm^{-2}nm^{-1}$)

$\bar{E}_{c\lambda}^{*}$ (600 nm) > $\frac{2 \times 10^{3}}{Y}$ J $s^{-1}cm^{-2}nm^{-1}$

($\frac{6 \times 10^{21}}{Y}$ photons $s^{-1}cm^{-2}nm^{-1}$)

Line Source (assuming $\Delta\lambda_{L}$ ~0.003 nm)

$\bar{E}_{L}^{*}$ (300 nm) > $\frac{25}{Y}$ J $s^{-1}cm^{-2}$

($\frac{4 \times 10^{19}}{Y}$ photons $s^{-1}cm^{-2}$)

E_{L}^{*} (600 nm) > $\frac{105}{Y}$ J $s^{-1}cm^{-2}$

($\frac{2 \times 10^{18}}{Y}$ photons $s^{-1}cm^{-2}$)

vii) spectral radiances of the xenon arc came from Gilbert (52); line radiances of electrodeless discharge lamps came from Mansfield et al. (53); line radiances of hollow cathodes came from Prugger et al. (54);

viii) all spectral radiances and line radiances of the three lasers (N_2- pumped dye laser, flashlamp pumped dye laser, and cw Ar^+ pumped dye laser) came from manufacturer's estimates (55, 56, 57) of (peak) power and spectral bandwidth; all laser beams are assumed to be expanded to a diameter of 0.5 cm;

ix) saturation spectral and line radiances were calculated from expressions given by Omenetto and Winefordner (40);

x) geometrical factors such as cell sizes, instrumental measurement factors, and modulation factors were chosen to be experimentally realistic for atomic fluorescence spectrometric systems, atomic emission spectrometric systems (similar to commercial flame and ICP systems) and atomic absorption spectrometric systems (with a narrow line source, similar to any commercial AA spectrometer; with a continuum source, an echelle grating spectrometer was assumed).

Observations and Conclusions

Several conclusions are apparent by comparing the limits of detection (in atoms/cm^3 of hot gases) and the S/N expressions used to estimate the limits of detection.

i) Atomic absorption flame spectrometric detection limits in any flame or plasma are in the range of 10^6 - 10^9

atoms/cm^3 for 300 nm resonance lines, and 10^5 - 10^7 atoms/cm^3 for 600 nm resonance lines.

ii) Using a line source in atomic absorption spectrometry, improves detection limits anywhere from 10X to 50X over the use of a continuum source.

iii) Atomic emission flame/plasma spectrometric detection limits are about equal to those of atomic absorption spectrometry using a continuum source at 300 nm (except for ICP) or lower wavelengths, and greater than 50X better for resonance lines at 600 nm or higher; ICP typically achieves detection limits in the range of 10^3 - 10^5 atoms/cm^3.

iv) Atomic fluorescence flame/plasma spectrometer detection limits with either narrow line or continuum conventional sources are typically 10^7 - 10^9 atoms/cm^3 for cases where "cell" background emission shot noise is dominant at 300 nm, and 10^5 - 10^8 at 600 nm. If the "cell" background emission can be made negligible and only dark current shot noise remains, then detection limits with either line or continuum conventional sources will be 10^2 - 10^5 atoms/cm^3 for 600 nm resonance lines, or 10^4 - 10^6 atoms/cm^3 for 300 nm resonance lines; the ICP and the H_2/O_2/Ar flame are much better cell environments for AF because of their much smaller quenching effects.

v) Atomic fluorescence flame/plasma spectrometric detection limits with laser continuum sources and saturation conditions result in superior values, i.e., detection limits in the 10^1 - 10^2 atoms/cm^3 range for the N_2-pumped

dye laser, in the 1 - 10^1 atoms /cm^3 range for the flashlamp pumped dye laser, and in the less than 1 atom/cm^3 range for the cw Ar^* dye laser assuming detector shot noise limitation and approximately 10^5, 10^4 and 10^1 atoms/cm^3 for background emission shot noise limitation for the three laser systems; background noise limited detection limits at 600 nm are always better than or equal to those at 300 nm because the noise level is generally less at 600 nm and signal levels are larger.

vi) Atomic fluorescence flame/plasma spectrometric detection limits with the cw Ar^+ pumped dye laser, under saturation conditions, are better than with the flashlamp pumped dye laser, which are better than with the N_2 - pumped dye laser because the duty factors for the three lasers are 0.5, 10^{-5} and 10^{-7} respectively. However, it should be noted that only the N_2 - pumped laser and flashlamp pumped dye laser beams can be beam expanded to approximately 0.5 cm diameter, and still approach saturation (see typical operating conditions in Table X) at 300 nm or even at 600 nm.

vii) Atomic fluorescence saturation limited flame/plasma spectrometric detection limits with the etalon narrowed N_2 - pumped dye lasers are better than the continuum cases; it is also clear that detection limits with a narrow line dye laser decrease linearly as the square root of the line source irradiance increases. Thus, it would appear that if more powerful line sources were utilized, one could expect to realize a further enhancement in detection limits. In

addition, in the case of resonance excitation, the ratio of fluorescence to fluorescence scatter will be considerably greater for a narrow line laser source than for a continuum laser source producing the same fluorescence signal level.

viii) Atomic fluorescence flame spectrometry using a low intensity continuum excitation source (flashlamp pumped dye laser) in an C_2H_2/Air flame exhibits a detection limit for two photon (600 nm) absorption via a real level one half that for a single photon (300 nm) absorption under similar conditions. This thereby confirms the fact that the two-photon process enhances selectivity only at the expense of sensitivity.

ix) For the case of two-photon (600 nm) absorption via a virtual level (no saturation possible) the gain in selectivity comes at a much higher price with respect to sensitivity. In this case, we observe a limiting observable concentration of 10^6 to 10^7 atoms/cm^3, whereas the one photon process can detect from 10^3 to 10^4 atoms/cm^3.

x) It should be stressed that detection limits in Tables VIII and IX are in atoms/cm^3 of hot gases and <u>not</u> in solution analyte concentration sprayed (nebulized) into the cell. If the process of conversion of analyte into species/cm^3 of hot gases is not efficient, it is possible for a technique such as laser excited AFS in a flame with a detection limit of 10^3 atoms/cm^3 and atomic emission ICP with a detection limit of 10^6 atoms/cm^3 to invert with respect to detection limits in solution. The rather impressive detection limits

(approximately 10^2 atoms/cm^3) by laser excited AFS have, however, been experimentally approached by Fairbanks et al. (58), by Smith et al. (59) and by Gelbwachs et al. (60). For the theoretical approach to calculating detection limits with respect to analyte concentration in solution from atoms/cm^3 in hot gases see Appendix I.

Analysis of Non-Photomultiplier Techniques

Atomic Flame Photoacoustic Spectroscopy (AFPS)

The final two techniques which we wish to calculate theoretical detection limits for are photoacoustic spectroscopy. Although these two techniques are not highly regarded as acceptable methods of practical trace metal analysis, a considerable amount of research is being focused upon them. Therefore, it seems as if, besides the conventional methods of trace metal analysis previously discussed, these newer techniques should be looked at with respect to their ultimate limits of detectability.

To begin with, we will discuss the analysis of gaseous species by AFPS. Although AFPS is more reknowned for the analysis of solids (61) and liquids (62) a considerable amount of work has been done studying the analysis of gaseous species (both in gas cells (63,64,65) and flame cells (66)). The approach to deriving signal and noise expressions for AFPS is similar to that taken for AAFS, AEFS and AFFS. However, due to fundamental differences in the modes of detection of analyte signal, there are some differences. A brief description of the signal producing and measurement steps

may prove beneficial to understanding the final equations.

In AFPS, the excitation of analyte is analagous to that of AAFS and AFFS; however that is where the similarity ends. In AAFS, we are interested in measuring the amount of light absorbed by an analyte, in AFFS our attention is focused on the amount of light fluoresced by the analyte and, in AFPS, we focus our attention on the translational energy produced by collisional de-excitation of the analyte species. The first two techniques establish quantitative relationships between analyte concentration and light energy, wheras AFPS relates translational energy (pressure) to concentration. The detection device most commonly used in AAFS, AEFS and AFFS is the photomultiplier tube, whereas AFPS utilizes a suitable pressure transducer, namely a microphone.

We are interested in measuring the signal generated by laser excitation of atoms introduced into a typical air/acetylene flame. This will be accomplished by monitoring the pressure wave resulting from the periodic analyte excitation with a condenser microphone. The analysis is based on the following assumptions:

i) all atoms that absorb the incident radiation will either return to their original ground state via radiational deactivation (fluorescence) or radiationless deactivation (quenching collisions);

ii) those atoms that return to the ground state via quenching collisions will do so by transferring their energy into translational energy of the flame gas molecules (67);

iii) this periodic energy conversion process (whose

frequency is determined by the frequency of the chopped light source) will in turn produce a pressure wave whose magnitude will remain constant until detected by the microphone which is located approximately 4 cm away from the flame border;

iv) the absolute limiting noise source is taken to be the equivalent noise pressure impinging upon the diaphragm of the microphone which is due to the Brownian motion of the local air molecules.

Although this final assumption does not fairly represent the limiting experimental noise sources, e.g., environmental noise pickup, chopper vibration pickup, flame background noise, flame temperature fluctuations,etc., it is assumed that with sufficient care and effort these experimental noises can, in principle, be eliminated leaving the limiting noise source to be that due to Brownian motion.

As mentioned for the cases of atomic spectroscopy using a photomultiplier detection schene, the following results will reflect the absolute best conditions possible for a typical photoacoustic experiment and will express the lowest possible detection limit the analyst can hope to achieve. The following is the derived expression for the signal produced (in units of energy per unit volume),

$$S = \frac{E_C(\lambda_o)}{\ell} \frac{\lambda_o^4}{8\pi c} \frac{g_u}{g_l} (1-Y) k_{21} n_T^L \beta \left(\frac{\Omega}{4\pi}\right) \ell \tau_i$$

where all the terms have been previously defined except for,

k_{21} = collisional rate constant for radiationless deactivation, s^{-1}

β = fraction of collisional energy that is transferred to translational energy of the gas molecules, dimensionless.

$\frac{\Omega}{4\pi}$ = fraction of 4π sr collected by the microphone, dimensionless

The limiting noise expression, as previously mentioned, will be derived from the Brownian motion of molecules impinging upon the diaphragm of the microphone and is expressed as follows,

$$N = \left(\frac{8k\ T\ m\ \Delta f}{M\ \tau_m} \right)^{\frac{1}{2}}$$

where,

k = Boltzmann's constant, erg K

T = temperature, K

m = mass per unit area of the diaphragm, g cm^{-2}

Δf = frequency interval about the measured frequency, Hz

M = area of diaphragm, cm^2

τ_m = damping time of the diaphragm, s

In order to evaluate the S/N expression, numerical values for the variables will be the same as those in Table X except where specified otherwise. The calculations were performed for atoms whose wavelength of excitation is centered at 300 nm and at 600 nm. We will look at a "typical" good absorber and weak fluorescer. The light source is the cw Ar^+ pumped dye laser. The microphone is represented by a B & K 4144 type condensor microphone. A

10 cm pathlength was chosen for the flame cell, while a total of 5×10^{-3} of the total amount of sound produced is collected when considering the geometry of the microphone.

The results of the calculations are given in Table XI. With respect to typical limits of detection reported in the literature ranging from 1×10^{7} to 1×10^{10} species/cm^3 (68,69), the results appear to be very reasonable.

Atomic Flame Optogalvanic Spectroscopy(AFOS)

Atomic flame optogalvanic spectroscopy has been shown to be another valuable method for measuring trace metals in flames (70,71,72). The fundamental principle of AFOS is the ionization of the analyte species and monitoring the current produced when the cell is in the midst of an applied voltage. In the derivation of the expression for the signal produced by AFOS, the experimental system used as a model was that of Travis et al. (73). They utilized a flame cell (air/acetylene) 10 cm long equipped with two parallel molybdenum plates as the ionization current measurement device. The source was a flashlamp pumped dye laser with a pulse width of 1×10^{-6} s. The limiting noise source was taken to be shot noise due to the inherent electron population of the flame. Four cases are to be examined, all of which are calculated for a typical atom whose absorption line is centered around 300 nm. The first two are those in which the atom has a high ionization rate constant (74) and high and low background noise levels. The last two cases are for a low ionization rate constant and the same varying background levels.

Table XI

Calculated Detection Limits for
Atomic Flame Photoacoustic Spectroscopy

Wavelength (nm)	Concentration (atoms/cm^3)
300	2.0×10^9
600	1.3×10^7

Table XII

Theoretical Limits of Detection for
Atomic Flame Optogalvanic Spectroscopy

Absorption Process	Concentration ($atoms/cm^3$) low background	high background
One photon		
$k_{2i} = 10^8\ s^{-1}$	5×10^6	5×10^7
$k_{2i} = 10^4\ s^{-1}$	5×10^{10}	5×10^{11}
Two photon		
virtual ($k_{3i} = 10^{12}\ s^{-1}$)	2×10^3	2×10^4
real ($k_{3i} = 10^{12}\ s^{-1}$)	3×10^{-5}	3×10^{-4}

The intensity expression is given as follows (in events),

$$S = D_S E_{PC\lambda}(\lambda_o) \frac{\lambda_o^4}{8\pi c} \frac{g_u}{g_l} n_T^L Y \ell H k_{2i} \tau_i$$

where all the variables have been previously defined except for the following,

ℓ = length of collector plates, cm

M = height of collector plates, cm

k_{2i} = ionization rate constant, s^{-1}

The background limiting shot noise (in events) due to the electron population of the flame is calculated via the following expression,

$$N = (2D_D \overline{R}_B \tau_i)^{\frac{1}{2}}$$

where,

$\overline{R}_B$ = average background count rate, events/s

If we assume a background current of 1 X 10^{-8}A for a low background flame and 1 X 10^{-6}A for a high background flame (41), a 10 s integration time and that the high ionization rate constant is 1 X 10^8 s^{-1} and the low ionization rate constant is 1 X 10^4 s^{-1}, we are now able to calculate the theoretical limits of detection for AFOS. The results can be found in Table XII. These results agree extremely well with those of Travis et al. (73) who estimated that their experimentally derived detection limits ranged from 1 X 10^6 atoms/cm^3 to 1 X 10^{10} atoms/cm^3.

In an analagous fashion to atomic fluorescence flame spectrometry, AFOS has been shown to gain certain advantages through the utilization of two-photon absorption processes. As in both cases, the two photon absorption process enhances the attractiveness of the techniques by enhancing their selectivity. However, due to the relatively weak absorptivities in the two photon process (via a virtual level) this enhancement cones only at the expense of sensitivity. Nevertheless, we shall consider the cases of two photon (600 nm) absorption via a virtual level and that via a real level for AFOS (Figure II). For the case of the two photon absorption via a virtual level, the S/N expression, assuming the same limiting background noise source, becomes,

$$\left(S/N\right)^{\text{2 photon, virtual}}_{\text{lim, BS}} = \frac{E_{CP}^{2}\,\Delta\tau_L\,\delta\,Y\,n_T^L\,A\,\ell\,k_{3i}\,\tau_i}{(2D_D\,\bar{R}_B\,\tau_i)^{\frac{1}{2}}}$$

For the case of a real intermediate level, the S/N expression is as follows,

$$\left(S/N\right)^{\text{2 photon, real}}_{\text{lim, BS}} = \frac{D_S\,\frac{n_T^L}{4}\,A\,\ell\,k_{3i}\,\tau_i}{(2D_D\,\bar{R}_B\,\tau_i)^{\frac{1}{2}}}$$

where all terms in the preceding two equations have been defined except,

$\Delta\tau_L$ = pulse width of the laser, s

k_{3i} = ionization rate constant from third level, s^{-1}

The term k_{3i} is derived from k_{2i} by the Boltzmann relationship,

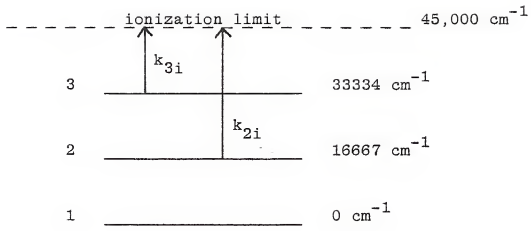

Figure II

Energy Level Diagram for a Hypothetical Atom
Undergoing Photoionization

$$k_{3i} \tilde{=} k_{2i} \frac{\exp(-\Delta E_{3i}/kT)}{\exp(-\Delta E_{2i}/kT)}$$

where ΔE_{3i} is the energy difference between level three and the ionization threshold (Figure II) and ΔE_{2i} is the energy difference between level two and the ionization threshold.

The results of the calculations are to be found in Table XII. With respect to the conventional one photon process, a two-photon absorption via a virtual level exhibits a detection limit three orders of magnitude better. However, the ultimate in sensitivity is seen for the two photon absorption via real levels. This is mainly due to the assumption of saturation of each transition which is theoretically appealing, although experimentally difficult to obtain.

APPENDIX A

DETECTION LIMITS BY ATOMIC SPECTROMETRIC METHODS FOR ANALYTES IN REAL SAMPLES

As previously discussed, in analytical atomic spectroscopy, it is necessary to convert the analyte in a sample into gaseous atoms (or ions) in order for atomic processes to be observed. One is therefore interested in the conversion factor, θ, from atoms/cm^3 of hot gases to µg/ml of sample solution assuming the sample is nebulized to produce the atomic vapor. The nebulization process is the most common means of sample introduction although electrothermal atomizers have widespread use as well. However, for reasons previously mentioned, they will not be discussed here.

The conversion factor, θ, is given by the following equation (41),

$$\theta = \frac{c}{n_T^L} = \frac{10^6 Q\, e_f\, M_A}{N_A\, F\, \varepsilon\, \beta_v\, \beta_a}, \quad \frac{\mu g/ml}{atoms/cm^3}$$

where the terms are defined as following;

c = solution concentration of analyte, µg/ml

n_T^L = limiting gaseous concentration of analyte, atoms/cm^3

M_A = atomic weight of analyte, g/mole

F = transport rate of sample solution as determined by the nebulizer, cm^3/s

ε = efficiency of nebulization and desolvation, dimensionless

β_v = efficiency of vaporization, dimensionless

β_a = efficiency of atomization, dimensionless

Q = flow rate of unburnt gases (at room temperature) into the flame, cm^3/s

e_f = flame gas expansion factor, dimensionless.

Therefore, to convert the estimated detection limits present throughout this work (from atoms/cm^3 to µg/ml) one just needs to multiply the tabular values by Θ.

A brief discussion concerning the variables involved may serve to exemplify their relationships to the Θ factor. For instance, ε can vary from approximately 0.01 to 0.1 depending upon the nebulizer chamber design (75) but is nearly independant of the flame/plasma being used for analysis. On the other hand, β_v depends critically (especially for cooler flames such as, C_2H_2/Air or H_2/O_2/Ar) upon the sample matrix, i.e., the chemical components and their relative concentrations to the analyte concentration, and upon the analyte chemical and physical properties. For hotter, more reducing combustion flames, as the C_2H_2/N_2O flame, and especially for the hot inert, ICP discharge, these problems are much less severe. Finally, the parameter β_a depends critically upon the thermodynamic characteristics of the analyte, the concentration of radicals, as O, OH, H, CN, CH etc., in the flame gases, and on flame temperature. Parsons et al. (48) have tabulated β_a values measured by a

number of researchers for a number of elements in several flames.

In order to estimate Θ values and the corresponding solution detection limits from flame detection limits, a few assumptions must be made. If we assume an C_2H_2/Air flame produced by 2 l/min of C_2H_2 and 10 l/min of air, then Q is 200 cm^3/s of flame gases at 2500 K (e_f = 8.5). Assuming a transport rate of 3 cm^3/min and an efficiency, ε, of 0.10, then $F(e_f)$ is 0.005 cm^3/s. Therefore,

$$\Theta = \frac{6 \times 10^{-13} M_A}{\beta_v \beta_a} .$$

For Mg (M_A = 23 amu), $\beta_v \beta_a \sim 1$ and so,

$$\Theta(Mg) = 2 \times 10^{-11}$$

Thus a detection limit of 10^6 atoms/cm^3 (as in AA) would become 0.02 ppb (ng/ml) in solution. If these calculated results are compared to experimentally derived limits of detection tabulated in Table XIII good agreement is observed. For instance, the calculated limit of detection of 0.02 ppb for Mg by atomic absorption spectrometry with a line source, is only one order of magnitude below that which is experimentally achievable. Furthermore, if we assume Θ to be 10^{-11} for any typical atom, then the theoretically calculated atomic emission flame spectrometry detection limits of 10^{-2} to 10^{-8} ppm favorably compare with the experimentally obtainable concentrations of 10^1 to 10^{-4} ppm.

Table XIII

Characteristic limits of Detection for
Several Atomic Spectrometric Techniques

Element	Concentration (µg/ml)				
	AFFSC	AFFSL	AEFS	AAFSC	AAFSL
Ag	1 E-3	1 E-4	2 E-2	2 E-1	5 E-4
Bi	2 E-0	5 E-2	2 E-0	4 E-0	5 E-2
Ca	1 E-1	2 E-2	1 E-4	3 E-2	2 E-3
Cd	8 E-2	1 E-6	2 E-0	1 E-2	1 E-2
Co	5 E-1	1 E-2	5 E-2	3 E-0	5 E-3
Cr	1 E+1	5 E-2	5 E-3	2 E-1	5 E-3
Ga	5 E-0	7 E-2	3 E-1	2 E-0	1 E-2
Mg	1 E-2	1 E-3	5 E-3	1 E-2	3 E-4
Pb	3 E-0	1 E-2	2 E-1	2 E-0	1 E-2
Tl	7 E-2	8 E-3	2 E-2	6 E-1	3 E-2
Zn	3 E-2	4 E-5	5 E+1	2 E-2	2 E-3

APPENDIX B

DEFINITION OF FLICKER FACTOR

The flicker factor, ξ, can easily be defined if one considers the spectral noise power for flicker noise which is given in terms of current fluctuations by,

$$S_{fl}(f) = \frac{K^2 \, i^2}{f} = \frac{K^2 \, \bar{R}^2 \, e^2}{f}$$

where,

f = frequency, Hz

K^2 = a constant describing the low frequency stability of the noise source, dimensionless

i = current associated with the noise source, A

R = measured rate associated with noise source, counts/s

e = elementary charge of electron, coulomb

Having determined K one can define the flicker factor ξ, for integrator measurements as,

$$\xi_i = 0.83 \, K.$$

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BIOGRAPHICAL SKETCH

Sam Bayer was born on May 14, 1957, in Bat-Yam, Israel. He attended public schools in New York City for his elementary and junior high school education. In September of 1971, he was accepted for admission into the Bronx High School of Science in Bronx, N.Y.. His undergraduate career began in September of 1973, and included the institutions of the City University of New York, Miami Dade Junior College, Florida International University, and the University of Florida. It was at the latter institution where he was awarded a Bachelor of Science in August of 1976. He enrolled in the graduate school at the University of Florida immediately thereafter, aspiring to receive his Ph.D. in analytical chemistry under the auspices of Dr. James D. Winefordner. It was during his graduate school days that he met and married Audrey Helene Gallin.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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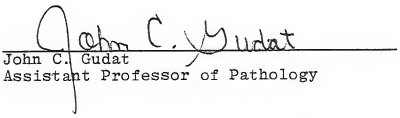

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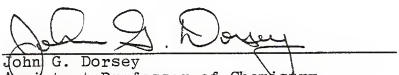

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